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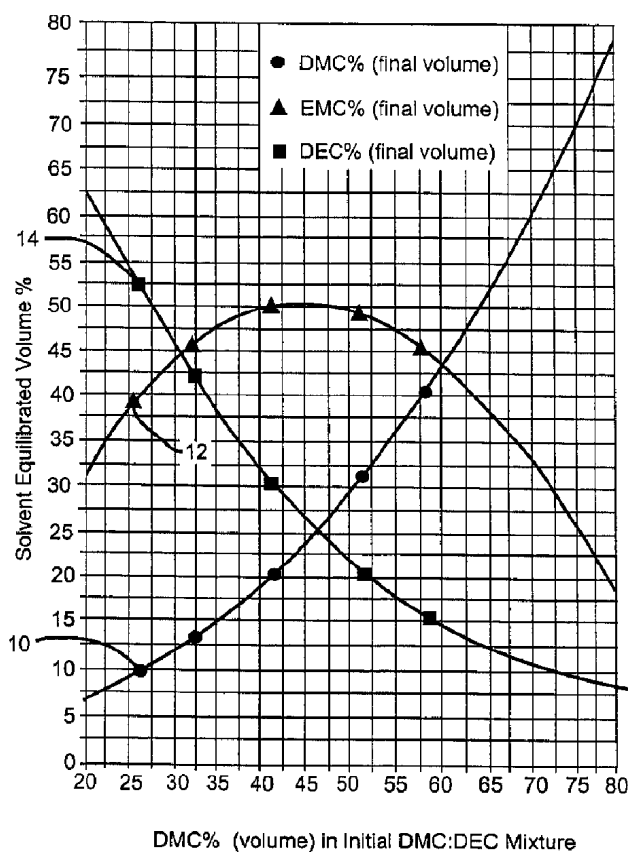
(71) Demandeur/Applicant:
WILSON GREATBATCH LTD., US

(72) Inventeurs/Inventors:
TAKEUCHI, ESTHER S., US;
GAN, HONG, US

(74) Agent: MACRAE & CO.

(54) Titre : ELECTROLYTES ORGANIQUES NON AQUEUX POUR LA DECHARGE A BASSE TEMPERATURE DE
PILES ELECTROCHIMIQUES RECHARGEABLES

(54) Title: NONAQUEOUS ORGANIC ELECTROLYTES FOR LOW TEMPERATURE DISCHARGE OF
RECHARGEABLE ELECTROCHEMICAL CELLS



(57) Abrégé/Abstract:

An alkali metal secondary electrochemical cell, and preferably a lithium ion cell, activated with an equilibrated quaternary solvent system, is described. The solvent system comprises a mixture of dialkyl carbonates and cyclic carbonates, and preferably a

(57) **Abrégé(suite)/Abstract(continued):**

quaternary mixture of dimethyl carbonate, diethyl carbonate, ethylmethyl carbonate and ethylene carbonate with dimethyl carbonate, diethyl carbonate and ethylmethyl carbonate in an equilibrated ratio. Lithium ion cells activated with this electrolyte have good room temperature cycling characteristics and excellent low temperature discharge behavior.

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ABSTRACT

An alkali metal secondary electrochemical cell, and preferably a lithium ion cell, activated with an
5 equilibrated quaternary solvent system, is described.
The solvent system comprises a mixture of dialkyl carbonates and cyclic carbonates, and preferably a quaternary mixture of dimethyl carbonate, diethyl carbonate, ethylmethyl carbonate and ethylene carbonate
10 with dimethyl carbonate, diethyl carbonate and ethylmethyl carbonate in an equilibrated ratio. Lithium ion cells activated with this electrolyte have good room temperature cycling characteristics and excellent low temperature discharge behavior.

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NONAQUEOUS ORGANIC ELECTROLYTES FOR LOW
TEMPERATURE DISCHARGE OF RECHARGEABLE
ELECTROCHEMICAL CELLS

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation in part of application Serial No. 09/133,799, filed August 13, 1998 which, in turn, claims priority based on U.S.
5 provisional application Serial No. 60/085,532, filed May 13, 1998.

BACKGROUND OF INVENTION

10 1. Field of the Invention

The present invention generally relates to the conversion of chemical energy to electrical energy, and more particularly, to a nonaqueous electrolyte
15 activating a rechargeable alkali metal electrochemical cell, particularly a lithium ion cell, designed for long cycle life and low temperature charge/discharge applications. These characteristics are provided, in part, by the activating electrolyte being a quaternary
20 mixture of dimethyl carbonate, diethyl carbonate, ethylmethyl carbonate and ethylene carbonate with the former three carbonates being in their equilibrated ratio.

25 2. Prior Art

Japanese patent application disclosure No. H8-162153 (Toshiba Battery Co.) relates to a secondary lithium ion battery activated with a mixed solvent
30 electrolyte of ethyl methyl carbonate (EMC), diethyl carbonate (DEC), dimethyl carbonate (DMC) and ethylene

carbonate (EC). The cell in this publication is stated to be capable of cycling at temperatures down to about -20°C. However, this Japanese patent application disclosure makes no mention of providing the constituents of DMC:EMC:DEC in an equilibrated mixture. The problem with this is that as the cell is cycled between a discharged and a charged state, the DMC and DEC undergo an ester exchange reaction to produce product EMC. If the ternary solvents of DMC:EMC:DEC are not filled into the cell in an equilibrated mixture, the cell performance will change as DMC and DEC react to form EMC or EMC disproportionates to form DMC and DEC. In that light, a cell that is initially rated for discharge at -20°C. may not be capable of such performance after several cycles as the percentage of DMC, DEC and EMC is changed. Such unpredictability is not acceptable in a lithium ion cell operating at such low temperatures.

According to the present invention, low temperature discharge and capacity fade problems are avoided by activating an alkali metal rechargeable cell, and particularly a lithium ion cell, with an equilibrated quaternary mixture of organic carbonate solvents in the electrolyte. The carbonate solvents comprising the quaternary mixture and the solvent mixture ratio are carefully selected to provide a lithium ion cell capable of discharge at temperatures below -20°C and that exhibits good cycling characteristics. At the same time, the cycleability of the present invention cells at room temperature is maintained as good as rechargeable cells of a similar electrode chemistry activated with the conventional binary carbonate solvent electrolytes.

SUMMARY OF THE INVENTION

The object of the present invention is, therefore, to improve the low temperature charge/discharge performance of lithium ion cells by activating them with an electrolyte comprising an equilibrated quaternary mixture of nonaqueous organic carbonate solvents. A further objective of the present invention is to provide such electrolytes in lithium ion cells to improve their cycle life in comparison to cells of a similar electrode chemistry activated with conventional binary carbonate and mixed carbonate/ester electrolytes.

For that purpose, the present invention is directed to an equilibrated quaternary mixed solvent system for an electrolyte activating a lithium ion cell, wherein the solvent system contains only organic carbonates. In particular, the preferred solvent mixture is EC:DMC:EMC:DEC, in which EC is in the range of about 20% to about 50%, DMC is in the range of about 12% to about 75%, EMC is in the range of about 5% to about 45% and DEC is in the range of about 3% to about 45%, by volume. This solvent system provides the cell with good low temperature discharge and cycling characteristics.

These and other objects of the present invention will become increasingly more apparent to those skilled in the art by reference to the following description and to the appended drawings.

DETAILED DESCRIPTION OF THE DRAWINGS

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Fig. 1 is a graph of equilibrated mixtures of DMC:EMC:DEC based on a starting mixture of DMC:DEC.

Figs. 2 to 5 are graphs constructed from the average discharge rate efficiency of various

rechargeable cells according to the prior art and the present invention discharged at room temperature, 0°C, -20°C and -40°C.

Fig. 6 is a graph constructed from the average
5 discharge efficiency of the cells discharged in Figs. 2 to 5 cycled at various temperatures.

Fig. 7 is a graph constructed from a lithium ion cell according to the present invention cycled at room temperature.

10 Fig. 8 is a graph constructed from a cycle results of a lithium ion cell according to the present invention discharged at various temperatures and under various rates.

15 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

A secondary electrochemical cell constructed according to the present invention includes an anode active material selected from Groups IA, IIA, or IIIB of
20 the Periodic Table of Elements, including the alkali metals lithium, sodium, potassium, etc. The preferred anode active material comprises lithium.

In secondary electrochemical systems, the anode electrode comprises a material capable of intercalating
25 and de-intercalating the alkali metal, and preferably lithium. A carbonaceous anode comprising any of the various forms of carbon (e.g., coke, graphite, acetylene black, carbon black, glassy carbon, etc.) which are capable of reversibly retaining the lithium species, is
30 preferred. Graphite is particularly preferred due to its relatively high lithium-retention capacity. Regardless of the form of the carbon, fibers of the carbonaceous material are particularly advantageous because the fibers have excellent mechanical properties

which permit them to be fabricated into rigid electrodes that are capable of withstanding degradation during repeated charge/discharge cycling. Moreover, the high surface area of carbon fibers allows for rapid
5 charge/discharge rates. A preferred carbonaceous material for the anode of a secondary electrochemical cell is described in U.S. Patent No. 5,443,928 to Takeuchi et al., which is assigned to the assignee of the present invention and incorporated herein by
10 reference.

A typical secondary cell anode is fabricated by mixing about 90 to 97 weight percent graphite with about 3 to 10 weight percent of a binder material which is preferably a fluoro-resin powder such as
15 polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), polyethylenetetrafluoroethylene (ETFE), polyamides and polyimides, and mixtures thereof. This electrode active admixture is provided on a current collector such as of a nickel, stainless steel, or
20 copper foil or screen by casting, pressing, rolling or otherwise contacting the active admixture thereto.

The anode component further has an extended tab or lead of the same material as the anode current collector, i.e., preferably nickel, integrally formed
25 therewith such as by welding and contacted by a weld to a cell case of conductive metal in a case-negative electrical configuration. Alternatively, the anode may be formed in some other geometry, such as a bobbin shape, cylinder or pellet to allow an alternate low
30 surface cell design.

The cathode of a secondary cell preferably comprises a lithiated material that is stable in air and readily handled. Examples of such air-stable lithiated cathode materials include oxides, sulfides, selenides,

and tellurides of such metals as vanadium, titanium, chromium, copper, molybdenum, niobium, iron, nickel, cobalt and manganese. The more preferred oxides include LiNiO_2 , LiMn_2O_4 , LiCoO_2 , $\text{LiCo}_{0.92}\text{Sn}_{0.08}\text{O}_2$ and $\text{LiCo}_{1-x}\text{Ni}_x\text{O}_2$.

5 Before fabrication into an electrode for incorporation into an electrochemical cell, the lithiated active material is preferably mixed with a conductive additive. Suitable conductive additives include acetylene black, carbon black and/or graphite.

10 Metals such as nickel, aluminum, titanium and stainless steel in powder form are also useful as conductive diluents when mixed with the above listed active materials. The electrode further comprises a fluoro-resin binder, preferably in a powder form, such as PTFE,

15 PVDF, ETFE, polyamides and polyimides, and mixtures thereof.

 To discharge such secondary cells, the lithium ion comprising the cathode is intercalated into the carbonaceous anode by applying an externally generated

20 electrical potential to recharge the cell. The applied recharging electrical potential serves to draw the alkali metal ions from the cathode material, through the electrolyte and into the carbonaceous anode to saturate the carbon comprising the anode. The resulting Li_xC_6

25 electrode can have an x ranging between 0.1 and 1.0. The cell is then provided with an electrical potential and is discharged in a normal manner.

 An alternate secondary cell construction comprises intercalating the carbonaceous material with the active

30 alkali material before the anode is incorporated into the cell. In this case, the cathode body can be solid and comprise, but not be limited to, such materials as manganese dioxide, silver vanadium oxide, copper silver vanadium oxide, titanium disulfide, copper oxide, copper

sulfide, iron sulfide, iron disulfide and fluorinated carbon. However, this approach is compromised by the problems associated with handling lithiated carbon outside of the cell. Lithiated carbon tends to react
5 with explosive results when contacted by air.

The secondary cell of the present invention includes a separator to provide physical segregation between the anode and cathode active electrodes. The separator is of an electrically insulative material to
10 prevent an internal electrical short circuit between the electrodes, and the separator material also is chemically unreactive with the anode and cathode active materials and both chemically unreactive with and insoluble in the electrolyte. In addition, the
15 separator material has a degree of porosity sufficient to allow flow therethrough of the electrolyte during the electrochemical reaction of the cell. The form of the separator typically is a sheet which is placed between the anode and cathode electrodes. Such is the case when
20 the anode is folded in a serpentine-like structure with a plurality of cathode plates disposed intermediate the anode folds and received in a cell casing or when the electrode combination is rolled or otherwise formed into a cylindrical "jellyroll" configuration.

25 Illustrative separator materials include fabrics woven from fluoropolymeric fibers of polyethylenetetrafluoroethylene and polyethylenechlorotrifluoroethylene used either alone or laminated with a fluoropolymeric microporous film.

30 Other suitable separator materials include non-woven glass, polypropylene, polyethylene, glass fiber materials, ceramics, a polytetrafluoroethylene membrane commercially available under the designation ZITEX (Chemplast Inc.), a polypropylene membrane commercially

available under the designation CELGAD (Celanese Plastic Company, Inc.) and a membrane commercially available under the designation DEXIGLAS (C.H. Dexter, Div., Dexter Corp.).

5 The choice of an electrolyte solvent system for activating an alkali metal electrochemical cell, and particularly a fully charged lithium ion cell is very limited due to the high potential of the cathode material (up to 4.3V vs. Li/Li⁺ for Li_{1-x}CoO₂) and the low
10 potential of the anode material (0.01V vs. Li/Li⁺ for graphite). Organic carbonates are generally used in the electrolyte solvent system for such battery chemistries because they exhibit high oxidative stability toward cathode materials and good kinetic stability toward
15 anode materials. Table 1 lists the physical properties of various carbonate solvents.

Table 1

20	Solvent	MP (°C)	BP (°C)	(25°C)	η (cP, 20°C)
	EC	36.4	238	95.3	1.85 (40°C)
	PC	-54.5	242	64.4	2.51
	BC	-53	240	53	3.2
	VC	22	162	---	---
25	DMC	3	90	3.12	0.59
	EMC	-55	109	---	0.66 (25°C)
	DEC	-43	127	2.82 (20°C)	0.75
	DPC	---	167	---	---
	MPC	-49	130	---	0.9
30	EPC	-81	148	---	0.92 (25°C)

From Table 1, it can be seen that the cyclic carbonates ethylene carbonate (EC) and vinylene

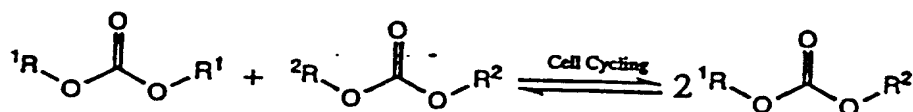
carbonate (VC) have melting points higher than 0°C, as described in U.S. Patent No. 5,712,059 to Barker et al. Therefore, while electrolytes prepared with these solvents perform well at room temperature, they may or
5 may not work well at lower temperatures due to electrolyte freezing. Instead, the high dielectric constant solvents propylene carbonate (PC) and butylene carbonate (BC) are preferred for low temperature applications due to their low melting points. However,
10 since those solvents can not passivate a graphite electrode during lithiation, they are not suitable for lithium ion cells comprising graphite as an anode active material. Thus, for graphite electrodes, EC and VC are still the best choice for use as the high dielectric
15 constant solvent components.

All linear carbonate solvents other than DMC have melting points lower than -40°C. Unfortunately, they also have higher viscosities than that of DMC. For example, although DEC has a relatively low melting point
20 of -43°C, that does not necessarily mean that an electrolyte prepared from DEC will result in high conductivity at low temperatures. S.T. Mayer, H.C. Yoon, C. Bragg, and J.H. Lee of PolyStor Corporation, presentation at *The Thirteenth International Seminar on
25 Primary and Secondary Battery Technology and Application*, March 4-7, 1996, Boca Raton, Florida describe electrolytes consisting of 1.39M LiPF₆/EC:DEC = 50:50 to 25:75 having freezing points higher than -15°C.

Therefore, in formulating a quaternary mixed
30 solvent system for an electrolyte activating a lithium ion cell designed for low temperature applications wherein the electrolyte is at an equilibrium condition after preparation and will not undergo significant chemical composition variation during cell cycling,

several factors are important. These included the oxidative stability of the constituent carbonate solvents, the chemical stability of the equilibrated solvent mixture, the passivation effect of the electrolyte towards a graphite electrode, the freezing point of the electrolyte and the increased low temperature conductivity of the electrolyte. For typically used high dielectric constant (cyclic carbonate) solvents, ethylene carbonate is better than vinylene carbonate. With low viscosity (linear carbonate) solvents, the smaller the molecular size, the lower the solvent viscosity within the same class of compounds. Thus, DMC is better than EMC which is better than DEC.

Another factor which affects the cycleability of a lithium ion cell is the electrolyte stability toward the anode and the cathode. It is known that the chemical composition of the electrolyte initially filled into the casing to activate the cell can undergo chemical reaction during charge/discharge cycling, as reported by E.S. Takeuchi et al., *J. Electrochem. Soc.* 144, 1944-1948, 1997, which is incorporated herein by reference. The reaction is represented in the following equation:



This phenomenon is largely avoided by starting with a carbonate solvent mixture which is already at an equilibration state. A method of preparing electrolytes of this type is fully described in U.S. Patent Nos. 5,962,720 and 6,057,062, both to Gan et al., which are

assigned to the assignee of the present invention and the discloses of which are incorporated herein by reference.

According to the present invention, suitable
5 nonaqueous electrolytes are comprised of an inorganic salt dissolved in a nonaqueous solvent and more preferably an alkali metal salt dissolved in a quaternary mixture of organic carbonate solvents comprising dialkyl (non-cyclic) carbonates selected from
10 dimethyl carbonate, diethyl carbonate, dipropyl carbonate (DPC), ethylmethyl carbonate, methylpropyl carbonate (MPC) and ethylpropyl carbonate (EPC), and mixtures thereof, and a cyclic carbonate selected from propylene carbonate (PC), ethylene carbonate, butylene
15 carbonate (BC) and vinylene carbonate (VC), and mixtures thereof. However, in a broader sense, the quaternary mixture of organic carbonate solvents comprises one cyclic carbonate and three linear carbonates, wherein of the three linear carbonates, a first one has the formula
20 R^1OCOOR^1 , a second one has the formula R^2OCOOR^2 and a third one has the formula R^1OCOOR^2 with R^1 and R^2 being different and being saturated or unsaturated organic groups containing 1 to 13 carbon atoms.

In a preferred form of the present invention, the
25 electrolyte activating the cell is at equilibrium with respect to the ratio of DMC:EMC:DEC. This is important to maintain consistent and reliable cycling characteristics. The reason for this is that it is known that due to the presence of low-potential (anode)
30 materials in a charged cell, an un-equilibrated mixture of DMC:DEC in the presence of lithiated graphite ($LiC_6 \sim 0.01$ V vs Li/Li^+) results in a substantial amount of EMC being formed. This phenomenon is described in detail in the previously referenced publication by E.S.

Takeuchi et al., *J. Electrochem. Soc.* 144, 1944-1948, 1997, which is incorporated herein by reference.

In particular, the above-referenced Takeuchi et al. publication describes the construction of test cells
5 having LiCoO_2 cathode material and petroleum coke anodes. Cycling of the cells with a 1.0 M $\text{LiPF}_6/\text{PC}:\text{DMC}:\text{DEC}=2:1:1$ electrolyte resulted in EMC formation. The product was observed even after only 1 charge cycle.

Takeuchi et al. then embarked on a study to
10 determine the effect of the cell components on the ester exchange reaction that produced EMC from DMC and DEC. To that end a solution of a one-to-one molar ratio of DMC and DEC was used. As summarized in Table 2 below, none of the cell active components (LiCoO_2 , petroleum coke,
15 and LiPF_6) catalyzed the ester exchange reaction upon stirring at room temperature for several days. Also, no new product was observed even when a substantial amount of HF was added to the reaction mixture. The results show that the ester exchange reaction was not initiated
20 or catalyzed by any of the individual cell components or an electrolyte acid impurity (HF). Similarly, additional tests indicated that the combination of all cell active components did not initiate the reaction. For example, when a fresh (uncharged) lithium-ion cell
25 was stored with added electrolyte, the exchange reaction did not occur. Therefore, Takeuchi et al. concluded that the exchange reaction of DEC and DMC to produce EMC is independent of the individual cell components and is dependent on the cell reactions which correlate to the
30 charged state of the cathode ($\text{Li}_{1-x}\text{CoO}_2$) and anode (Li_xC_6).

Takeuchi et al. then concluded that due to the presence of both high-potential (cathode) and low-potential (anode) materials in a charged test cell, it was impossible to distinguish which electrode is

responsible for initiating the ester exchange reaction by just examining the products of the full lithium-ion cell. To distinguish between the oxidative and reductive pathways, charged electrode materials were added individually to solutions of a one-to-one molar ratio of DMC and DEC. After storage under stirring for several days at room temperature, the reaction mixture containing chemically produced cathode material ($\text{Li}_{0.5}\text{CoO}_2$, 4.28 V vs. Li/Li^+) presented no sign of EMC formation. However, the reaction mixture containing lithiated graphite ($\text{LiC}_6 \sim 0.01$ V vs. Li/Li^+) showed a substantial amount of EMC formation (Table 2). Since the reaction occurs heterogeneously on the carbon surface, quantitative analysis of the reaction kinetics was not determined due to the uncertainty of the active surface area of the catalyst. Qualitatively, the longer the storage time under stirring, the more EMC was detected. The results demonstrate that the ester exchange reaction in lithium-ion cells is initiated at the anode (charged state). To confirm that the ester exchange reaction is catalyzed at a low potential, lithium metal was used in place of lithiated graphite. Similar results were obtained in that EMC was detected in the reaction mixture (Table 2).

25

30

TABLE 2

	<u>Catalyst</u>	<u>EMC detection (m/o)</u>
	LiCoO ₂	None
	Petroleum coke	None
5	LiPF ₆	None
	HF	None
	Li _{0.5} CoO ₂	None
	LiC ₆	39%
	Lithium	23%
10	SmI ₂	50%
	LiI	0.02%
	Li ₂ CO ₃	None
	LiOH	0.03%
15	LiOCH ₃	50%

From this it can be concluded that if DMC, DEC and EMC are not provided in a new lithium ion secondary cell built in a discharged condition, as is typically the case, those carbonate constituents will not readily equilibrate until the cell is charged and a lithiated carbonaceous material is formed at the negative electrode. As set forth in Table 2 above, lithiated carbon is a catalyst for the ester exchange reaction between DMC and DEC to form EMC. Also, the more charge/discharge cycles the cell undergoes, the more EMC which is produced until the carbonaceous negative electrode becomes passivated.

Fig. 1 is a graph showing various equilibrated mixtures of DMC:EMC:DEC based on a starting ratio of DMC:DEC. Five equilibrated mixtures are shown in the legend. For example, reading from left to right on the x-axis or abscissa of Fig. 1, the data point 10 for DMC

% (volume) in an initial DMC:DEC mixture is about 26% DMC. This means that an exemplary starting mixture of DMC:DEC begins as about 26% DMC:74% DEC. This starting mixture equilibrates to a mixture (read on the y-axis or ordinate) of about 9.5% DMC, 38.5% EMC (data point 12) and 52% DEC (data point 14) for mixture 1. This equilibrated mixture and those of mixtures 2 to 5 shown in the graph of Fig. 1 are set forth in Table 3 below.

10

TABLE 3

DMC% (volume) in			Resulting Equilibrated <u>Mixture of DMC: EMC: DEC</u>
	initial DMC:DEC		
<u>Mixture</u>	<u>Mixture</u>		
15	1	26:74	9.5:38.5:52
	2	34.5:65.5	13:44.5:42.5
	3	41:59	20:50:30
	4	52:48	31:49:20
	5	58:42	40:45:15

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Thus, according to the present invention in formulating a quaternary mixed solvent system for an electrolyte activating a lithium ion cell according to the present invention, it is important that DMC, EMC and DEC are at an equilibrium condition from the beginning so that the electrolyte does not undergo significant chemical decomposition during cell cycling.

Interestingly, the Japanese patent application disclosure JP 8-162153 referenced in the Prior Art section, relates to a secondary lithium ion battery activated with a mixed solvent electrolyte of ethyl methyl carbonate, diethyl carbonate, dimethyl carbonate and ethylene carbonate. Paragraph 0017 of JP 8-162153

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teaches an electrolyte solution for an assembled battery which includes ethyl methyl carbonate, dimethyl carbonate, dimethyl carbonate and ethylene carbonate mixed together in a weight ratio of 45:35:10:10. It is known that the density of ethylene carbonate is 1.41 g./ml. at 20°C., the density of dimethyl carbonate is 1.07 g./ml. at 20°C., the density of ethyl methyl carbonate is 1.00 g./ml. at 20°C., and the density of diethyl carbonate is 0.97 g./ml. at 20°C. Based on the density of the various carbonate materials, an electrolyte having a weight ratio of EMC:DEC:DMC:EC = 45:35:10:10 is calculated to have a volume ratio of EMC:DEC:DMC:EC = 45.0:36.1:9.3:7.1, which calculates to a volume ratio of EMC:DEC:DMC = 49.8:39.9:10.3. This is not a equilibrated mixture of EMC:DEC:DMC, as evidenced by the previously referenced Fig. 1.

Paragraph 0023 of JP 8-162153 teaches a mixed solvent for activating a lithium-ion secondary battery having EMC:DEC:DMC:EC in a weight ratio of 55:25:10:10. As before, an electrolyte having a weight ratio of EMC:DEC:DMC:EC = 55:25:10:10 is calculated to have a volume ratio of EMC:DEC:DMC:EC = 55.0:25.8:9.3:7.1, which calculates to a volume ratio of EMC:DEC:DMC = 61.0:28.6:10.3. This is not an equilibrated mixture of EMC:DEC:DMC, as evidenced by the previously referenced Fig. 1.

The reason an equilibrated mixture of DEC, DMC and EMC is so important is that the cell described in JP 8-162153 is stated to be capable of cycling at temperatures down to about -20°C. As previously discussed, as the cell is cycled between a discharged and a charged state, the DMC and DEC undergo an ester exchange reaction to produce product EMC. Also, EMC disproportionates to DMC and DEC during cell cycling.

If the ternary solvents of DMC:EMC:DEC are not filled into the cell in an equilibrated mixture, the cell performance changes as DMC and DEC react to form EMC, and EMC disproportionates to form DMC and DEC. In that
5 light, a cell which is initially rated for discharge at, for example, -20°C . would not be capable of such performance after several cycles as the ratio of EMC:DMC:DEC changes in an ester exchange reaction or a disproportionation reaction. Such unpredictability is not
10 acceptable in a lithium ion cell.

After the constituents EMC, DMC and DEC are provided in the electrolyte in a equilibrated ratio, ethylene carbonate is added to tailor the cell to a particular application.

15 Preferred volume percent ranges for the various carbonate solvents include EC in the range of about 10% to about 50%; DMC in the range of about 5% to about 75%; EMC in the range of about 5% to about 50%; and DEC in the range of about 3% to about 45%. Electrolytes
20 containing this quaternary carbonate mixture exhibit freezing points below -50°C , and lithium ion cells activated with such mixtures have very good cycling behavior at room temperature as well as very good discharge and charge/discharge cycling behavior at
25 temperatures below -20°C .

Known lithium salts that are useful as a vehicle for transport of alkali metal ions from the anode to the cathode, and back again include LiPF_6 , LiBF_4 , LiAsF_6 , LiSbF_6 , LiClO_4 , LiAlCl_4 , LiGaCl_4 , $\text{LiC}(\text{SO}_2\text{CF}_3)_3$, LiNO_3 ,
30 $\text{LiN}(\text{SO}_2\text{CF}_3)_2$, LiSCN , $\text{LiO}_3\text{SCF}_2\text{CF}_3$, $\text{LiC}_6\text{F}_5\text{SO}_3$, LiO_2CCF_3 , LiSO_3F , $\text{LiB}(\text{C}_6\text{H}_5)_4$, LiCF_3SO_3 , and mixtures thereof. Suitable salt concentrations typically range between about 0.8 to 1.5 molar.

The assembly of the cell described herein is preferably in the form of a wound element cell. That is, the fabricated cathode, anode and separator are wound together in a "jellyroll" type configuration or "wound element cell stack" such that the anode is on the outside of the roll to make electrical contact with the cell case in a case-negative configuration. Using suitable top and bottom insulators, the wound cell stack is inserted into a metallic case of a suitable size dimension. The metallic case may comprise materials such as stainless steel, mild steel, nickel-plated mild steel, titanium or aluminum, but not limited thereto, so long as the metallic material is compatible for use with components of the cell.

The cell header comprises a metallic disc-shaped body with a first hole to accommodate a glass-to-metal seal/terminal pin feedthrough and a second hole for electrolyte filling. The glass used is of a corrosion resistant type having up to about 50% by weight silicon such as CABAL 12, TA 23, FUSITE 425 or FUSITE 435. The positive terminal pin feedthrough preferably comprises molybdenum although titanium, aluminum, nickel alloy, or stainless steel can also be used. The cell header comprises elements having compatibility with the other components of the electrochemical cell and is resistant to corrosion. The cathode lead is welded to the positive terminal pin in the glass-to-metal seal and the header is welded to the case containing the electrode stack. The cell is thereafter filled with the electrolyte solution described hereinabove, and hermetically sealed such as by close-welding a stainless steel ball over the fill hole, but not limited thereto. This above assembly describes a case-negative cell which is the preferred construction for the exemplary

secondary cell of the present invention. As is well known to those skilled in the art, the electrochemical system of the present invention can also be constructed in a case-positive configuration.

5 The following examples describe the manner and process of an electrochemical cell according to the present invention, and they set forth the best mode contemplated by the inventors of carrying out the invention, but they are not to be construed as limiting.

10

EXAMPLE I

Carbonate Solvent Mixture Preparation

1. Mixture 1 Synthesis

15

A 2:1 molar ratio (volume ratio of 58:42) of DMC (116 ml) and DEC (84 ml) was mixed in a 500 ml flask. A catalyst of 0.1g LiOCH_3 was added to the mixture which was then refluxed for 12 hours. Gas chromatography (GC) analysis indicated that the reaction mixture reached equilibration with a DMC:EMC:DEC volume ratio of 40:45:15. The reaction mixture was then filtered through 47 mm of a Glass Fiber Filter, Type A/E (from Gelman Science). Clear solution (Mixture 1) was
20
25 obtained.

2. Mixture 2 Synthesis

A 1:1 molar ratio (volume ratio 41:59) of DMC (82 ml) and DEC (118 ml) was mixed in a 500 ml flask. A catalyst of 0.1g LiOCH_3 was added to the mixture which was then refluxed for 12 hours. Gas chromatography (GC) analysis indicated that the reaction mixture reached equilibration with a DMC:EMC:DEC volume ratio of
30

20:50:30. The reaction mixture was then filtered through 47 mm of a Glass Fiber Filter, Type A/E (from Gelman Science). Clear solution (Mixture 2) was obtained.

5 The above examples demonstrate a synthetic method. The final volume ratio of the equilibrated solvent mixture can be adjusted by varying the ratio of the initial solvent constituents. For example, the ratio of EMC in the final reaction mixture can range from about
10 41% to about 48% for starting ratios of DMC:DEC of about 4:2 to 2:4, respectively. As is apparent to those skilled in the art, the solvent mixtures can also be prepared by mixing the appropriate amount of pure DMC, EMC and DEC.

15

EXAMPLE II

Electrolyte Preparation and Their Properties

20 Eight new electrolytes were prepared by mixing EC with Mixture 1 or Mixture 2 in the volume ratio of 2:8, 3:7, 4:6, and 5:5. A conventional electrolyte was also prepared for comparison, as summarized in Table 4.

25

Table 4

Electrolyte	[LiAsF ₆]	[LiPF ₆]	Solvent Ratio
	M	M	EC:DMC:EMC:DEC
1	1.0		20:32:36:12
2	1.0		30:28:32:10
30 3	1.0		40:24:27:9
4	1.0		50:20:23:7
5	1.0		20:16:40:24
6	1.0		30:14:35:21

7	1.0		40:12:30:18
8	1.0		50:10:25:15
9		1.0	30:70

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The conductivity of these electrolytes was recorded at temperatures ranging from -20°C to 50°C with a YSI Model 32 Conductivity Meter. The results are summarized in Table 5.

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Table 5
Electrolyte Conductivity (mS)

Electrolyte	-20°C	-10°C	0°C	10°C	20°C	30°C	40°C	50°C
1	3.04	4.22	5.59	6.95	8.59	10.01	11.80	13.35
2	2.71	4.13	5.64	7.06	8.91	10.72	12.38	14.07
3	2.71	3.93	5.40	7.20	8.96	10.87	12.80	14.76
4	2.32	3.51	4.98	6.73	8.55	10.65	12.75	14.89
5	2.73	3.70	4.94	6.55	7.98	9.45	10.87	12.25
6	2.73	3.81	5.13	6.60	8.33	10.12	11.82	13.62
7	2.45	3.68	5.06	6.73	8.45	10.25	12.00	13.93
8	Freeze	3.48	4.77	6.35	8.23	10.18	12.19	14.23
9	Freeze	5.19	6.90	8.79	10.74	12.72	14.62	16.48

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The above results show that the conventional electrolyte 9 presented higher conductivities than that of the new formulated electrolytes at all temperatures, except at -20°C. At -20°C, electrolyte 9 froze, which makes it unusable. Unexpectedly, electrolyte 8 also froze at -20°C, however, electrolyte 4 which contained 50%, by volume, EC, as did electrolyte 8, did not freeze at the same temperature. Comparing these two electrolytes, electrolyte 4 contained more DMC (MP of 3°C) and less DEC (MP of -43°C) than that of electrolyte 8. This demonstrates that the electrolyte freezing point of a quaternary carbonate is not directly

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proportional to the percentage of the lowest melting point solvent component. The conductivity results also indicate that at low temperatures, electrolyte conductivity is inversely proportional to the EC percentage. In other words, the lower the EC percentage, the higher the electrolyte conductivity. Additionally, in comparing electrolytes having similar percentages of EC, electrolyte conductivity is proportional to the DMC concentration (electrolytes 1 vs. 5; 2 vs. 6; 3 vs. 7; 4 vs. 8). This is consistent with the consideration that the smaller the linear carbonate molecular size, the lower the solvent viscosity and the higher the electrolyte conductivity.

The freezing points of the above electrolytes 1 to 9 were also investigated and summarized in Table 6.

Table 6
Electrolyte Freezing Point Evaluation

	Electrolyte	Freezing Point
	1	-55°C < -50°C
	2	-60°C < -55°C
	3	<-32°C
	4	-25°C
	5	-75°C < -60°C
	6	-75°C < -60°C
	7	<-32°C
	8	-15°C
	9	-11°C

The above test results demonstrate that electrolytes 8 and 9 can not be used in lithium ion cells for low temperature (<-15°C) applications. All of

the other electrolytes can be used in lithium ion cells at or below -20°C .

EXAMPLE III

5 Lithium Ion Cell Preparation and Electrochemical Testing

1. Cell Preparation

The cathode was prepared by casting a LiCoO_2 cathode mixture on aluminum foil. The cathode mix contained 91% LiCoO_2 , 6% graphite additive and 3% PVDF binder. The anode was prepared similarly by casting an anode mixture containing 91.7% graphite and 8.3% PVDF binder on a copper foil. An electrode assembly was obtained by placing one layer of polyethylene separator between the cathode and the anode and the assembly was spirally wound into a jellyroll configuration and housed inside of an AA sized cylindrical stainless steel casing. Various groups of AA cells were obtained by activating the electrode assemblies with six different electrolytes, as shown in Table 7.

Table 7

Group	Electrolyte ()	of cells
1	1.0M $\text{LiPF}_6/\text{EC}:\text{DMC} = 30:70$ (#9)	5
2	1.0M $\text{LiAsF}_6/\text{EC}:\text{DMC} = 30:70$	5
3	1.0M $\text{LiAsF}_6/\text{EC}:\text{DMC}:\text{EMC}:\text{DEC} = 20:16:40:24$ (#5)	5
4	1.0M $\text{LiAsF}_6/\text{EC}:\text{DMC}:\text{EMC}:\text{DEC} = 30:14:35:21$ (#6)	4
5	1.0M $\text{LiAsF}_6/\text{EC}:\text{DMC}:\text{EMC}:\text{DEC} = 20:32:36:12$ (#1)	4
6	1.0M $\text{LiAsF}_6/\text{EC}:\text{DMC}:\text{EMC}:\text{DEC} = 30:28:32:10$ (#2)	5

2. Room Temperature Cycling Test

The thusly fabricated cells were charge/discharge cycled between 4.1V and 2.75V under a 0.14C discharge rate (1C rate = 520 mA) at room temperature. The cells were charged under a 0.14C rate to 4.1V and then the cells were held at that voltage until the current dropped to 10% of the original current. The cycling results of each group of cells are summarized in Table 8.

Table 8

Group*	Discharge Capacity (mAh)			Capacity Retention (%) at 50th Cycle	
	Cycle 1	Cycle 10	Cycle 50	vs. Cycle 1	vs. Cycle 10
1	545	510	461	84.6	90.4
2	530	505	461	87.0	91.3
3	525	507	464	88.4	91.5
4	525	498	462	88.0	92.8
5	520	492	453	87.1	92.1
6	538	512	478	88.8	93.4
*Data for groups 1, 2, 3 and 6 are the average of 5 cells. Data for groups 4 and 5 are the average of 4 cells.					

As set forth in Table 8, all six groups of cells exhibited similar cycling characteristics. In particular, the groups 3 to 6 cells activated with an electrolyte comprising a quaternary mixture of nonaqueous organic carbonate solvents according to the present invention presented similar cycling performance as that of the groups 1 and 2 cells with conventional binary solvent electrolytes.

3. Discharge Rate Capability at Various Temperatures

After the cycling test, the AA cells were charged at room temperature, then they were discharged under various C-rates at room temperature, 0°C, -20°C and -40°C. Three cells were used in each of the tests except for the room temperature test which used five cells. Assuming a room temperature discharge rate capacity of 0.14C as a 100% standard, the relative discharge efficiencies of all the other discharge conditions were calculated. The results are shown in Figs. 2 to 5 and summarized in Tables 9 to 12, respectively.

Table 9

Group		Discharge Rate Efficiency at Room Temperature(%) *						
		2.23C	1.12C	0.56C	0.28C	0.14C	0.07C	0.03C
15	1	32.7	82.4	95.5	98.8	100.0	-	-
	2	39.4	86.3	95.5	98.7	100.0	-	-
	3	20.4	69.0	93.6	98.1	100.0	-	-
	4	24.3	73.3	94.7	98.6	100.0	-	-
	5	28.5	78.7	94.5	98.3	100.0	-	-
20	6	30.4	84.7	96.3	98.9	100.0	-	-
* Average data of 5 cells. 1C rate = 520 mA discharge rate								

Table 10

25	Group	Discharge Rate Efficiency at 0 °C (%)*						
		2.23C	1.12C	0.56C	0.28C	0.14C	0.07C	0.03C
30	1	-	55.6	84.8	91.0	93.2	94.5	-
	2	-	54.5	81.9	89.6	92.8	94.5	-
	3	-	34.7	75.8	89.7	93.8	95.5	-
	4	-	38.8	75.4	89.0	93.2	95.0	-
	5	-	43.4	80.9	90.0	93.3	94.8	-
	6	-	46.8	84.5	91.8	94.3	95.4	-
* Average data of 3 cells. 1C rate = 520 mA discharge rate.								

Table 11

Group	Discharge Rate Efficiency at -20 °C(%) *						
	2.23C	1.12C	0.56C	0.28C	0.14C	0.07C	0.03C
1	-	-	4.6	6.0	6.7	7.4	8.5
2	-	-	3.6	4.9	5.7	6.4	7.7
3	-	-	9.2	66.0	85.3	91.2	94.7
4	-	-	12.0	61.7	79.7	87.8	92.8
5	-	-	25.2	72.8	86.5	91.0	93.7
6	-	-	26.2	71.5	85.5	90.5	93.7
* Average data of 3 cells. 1C rate = 520 mA discharge rate.							

Table 12

Group	Discharge Rate Efficiency at -40 °C(%) *						
	2.23C	1.12C	0.56C	0.28C	0.14C	0.07C	0.03C
1	-	-	0.0	0.0	0.0	0.0	0
2	-	-	0.0	0.0	0.0	0.0	0
3	-	-	0.0	0.1	2.7	29.7	72
4	-	-	0.0	0.0	0.0	0.1	7.5
5	-	-	0.0	0.2	6.2	49.5	80.6
6	-	-	0.0	0.0	0.0	3.1	71.5
* Average data of 3 cells. 1C rate = 520 mA discharge rate.							

In Fig. 2, respective curves 20, 22, 24, 26, 28 and 30 were constructed from the average discharge rate efficiency of the groups 1 to 6 cells at room temperature. Fig. 2 demonstrates that the groups 1 and 2 prior art cells activated with binary solvent electrolytes afforded better discharge rate capability than that of the groups 3 to 6 present invention cells at room temperature under discharge rates greater than >0.5C. At discharge rates lower than 0.5C, all groups of cells presented similar discharge efficiency.

In Fig. 3, respective curves 32, 34, 36, 38, 40 and 42 were constructed from the average discharge rate efficiency of the groups 1 to 6 cells at 0°C. Fig. 3 demonstrates that the groups 1 and 2 prior art cells
5 activated with binary solvent electrolytes still afforded better discharge rate capability than that of the groups 3 to 6 present invention cells at 0°C under a discharge rate greater than >0.5C. At a discharge rate lower than 0.5C, all groups of cells presented similar
10 discharge efficiency.

In Fig. 4, respective curves 44, 46, 48, 50, 52 and 54 were constructed from the average discharge rate efficiency of the groups 1 to 6 cells at -20°C. Fig. 4 demonstrates that at -20°C, the groups 1 and 2 prior art
15 cells activated with the binary solvent electrolytes afforded no realistic discharge capacity. This is consistent with the observation that electrolyte 9 freezes at -11°C. In contrast, the groups 3 to 6 cells activated with a quaternary mixture of nonaqueous
20 organic carbonate solvents according to the present invention delivered good discharge efficiencies under all rates tested. The results also demonstrate that the groups 5 and 6 cells activated with the present invention electrolytes 1 and 2 appear to have higher
25 discharge rate capability than that of the groups 3 and 4 cells activated with present invention electrolytes 5 and 6.

In Fig. 5, respective curves 56, 58, 60, 62, 64 and 66 were constructed from the average discharge rate efficiency of the groups 1 to 6 cells at -40°C. At that
30 temperature, none of the cells from groups 1 to 6 was capable of delivering any appreciable capacity above the 0.1C discharge rate. Under a lower discharge rate, the groups 1 and 2 prior art cells still were not capable of

delivering any appreciable capacity. In contrast, the groups 3, 5 and 6 present invention cells presented fairly high discharge efficiencies.

The test results in this example clearly demonstrate the effect of electrolyte chemistry has on lithium ion cell discharge efficiency at low temperatures. Cells activated with electrolytes comprising a quaternary mixture of nonaqueous organic carbonate solvents according to the present invention gave comparable discharge capacity at room temperature and 0°C with respect to cells of a similar electrode chemistry activated with prior art electrolytes. In addition, they provide superior discharge rate at capability over the cells with the conventional binary solvent electrolytes at or below -20°C. At or below -20°C, the groups 1 and 2 prior art cells cannot be discharged.

EXAMPLE IV

Charge/Discharge Cycling at Low Temperatures

After low temperature discharge rate capability tests, the cells constructed in Example III were cycle tested at 0°C and -20°C under a discharge rate of 0.14C. Since the groups 1 and 2 prior art cells are known to be incapable of discharging at -20°C, they were only tested at room temperature and at 0°C. All other groups of cells were tested at room temperature, 0°C and -20°C.

The groups 1 and 2 prior art cells were first cycled three times at room temperature. Then, they were equilibrated at 0°C for 24 hours before cycling for another three times. Finally, they were cycled three more times at room temperature. For the groups 3 to 6 present invention cells, similar procedures were used

except that before the 0°C test, the cells were tested at -20°C.

Assuming a room temperature first discharge cycle capacity as a 100% standard, the efficiencies of all other cycles were calculated. The results are summarized in Fig. 6, wherein respective curves 68, 70, 72, 74, 76 and 78 were constructed from the average discharge efficiency of the group 1 to 6 cells. For all groups of cells, about 95% of room temperature discharge capacity was realized at 0°C cycling. For the groups 3 and 4 cells, about 70% of room temperature discharge capacity was realized at -20°C cycling. For the groups 5 and 6 cells, about 75% of room temperature discharge capacity was realized at -20°C. The results illustrate that lithium ion cells activated with an electrolyte comprising a quaternary mixture of nonaqueous organic carbonate solvents according to the present invention are capable of being charge/discharge cycled at low temperature with good capacity efficiency.

EXAMPLE V

Self-Discharge and the Rate of Capacity Recovery

After the room temperature discharge rate capability test described in Example III, section 3, two cells from each of groups 1, 2, 3 and 6 and one cell from groups 4 and 5 were placed on self-discharge test. The cells were cycled between 4.1V and 2.75V once under a 0.14C discharge rate (defined as a first cycle), followed by charging them to the fully charged state (defined as a second cycle-charging). Then, the cells were stored on open circuit at room temperature for 30 days, followed by discharging (defined as a second cycle after storage-discharging). The cells were then cycled

once more (defined as a third cycle). The self-discharge rate was calculated from the ratio of the capacity difference between the first cycle discharge and the second cycle after storage-discharge over the first cycle discharge capacity. The rate of capacity recovery was calculated from the ratio of the third cycle discharge capacity divided by the first cycle discharge capacity. The results are summarized in Table 13.

Table 13
Self-Discharge and Recovery Rate of Capacity

Group	Self-Discharge (%)	Capacity Recovery (%)
1*	18.8	86.7
2*	13.8	91.0
3*	13.0	90.3
4	14.2	88.9
5	19.1	82.3
6*	13.1	90.3
	*Average data of two cells.	

The data in Table 13 indicates that other than the group 5 cells which exhibited a self-discharge rate similar to that of the group 1 prior art cells, all of the other groups of cells exhibited a lower self-discharge rate than that of the group 1 cells. The same trend was also observed for the capacity recovery rate. This example demonstrates that lithium ion cells activated with an electrolyte comprising a quaternary mixture of nonaqueous organic carbonate solvents according to the present invention present similar or lower self-discharge rates relative to that of cells

activated with a binary solvent electrolyte according to the prior art. The capacity recovery rate after self-discharge test is also comparable among all groups of cells.

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EXAMPLE VI

Two lithium ion cell were constructed having a cathode and an anode prepared as described in Example
10 III. The electrode assembly for each cell was spirally wound into a jellyroll configuration and housed inside a prismatic stainless steel casing. Prismatic lithium ion cells with initial capacity of 1.5 Ah were obtained by activating the electrode assemblies with an electrolyte
15 of 1.4M LiPF_6 /EC:DMC:EMC:DEC = 20:40:30.4:9.6, by volume.

Test 1

One of the lithium ion cells was charge-discharge cycled at room temperature. For all cycles, the cell
20 was charged under a 300 mA current to 4.1V until the current dropped to 60 mA. After one hour rest at open circuit, the cell was discharged under either a 300 mA current (cycles 1 to 65) or 1.5 Amp current (cycles 66 to 600) to 2.75V. After discharge, the cell was rested
25 on open circuit for one hour before the next cycle. The cycling results are illustrated in Fig. 7, curve 80. The results indicate that lithium ion cells activated with the quaternary solvent electrolyte of the present invention cycled well at room temperature. About 70% of
30 the initial capacity (the very first cycle) was maintained after 600 cycles under a 1C discharge rate.

Test 2

The other of the lithium ion cells built for this example was cycled under various conditions. The charging conditions were the same as those described in Test 1. However, the discharge conditions varied as follows:

- a) Formation Cycling: For cycles 1 to 5, the cell was discharged under a 300 mA current to 2.75V. A one hour rest period was provided between charging and discharging.
- b) Discharge Rate Capability Test: For cycles 6 to 9, the cell's discharge rate capabilities were tested by discharging the cell under a 300 mA current (0.2C rate), a 0.75 mA current (0.5C rate), a 1.5 Amp current (1.0C rate), and a 3.0 Amp current (2.0C rate). The results of this test are summarized in Table 14 and illustrated in Fig. 8. In Fig. 8, curve 82 is the results of cycles 1 to 9. The discharge capability was calculated based on the 0.2C rate as 100% efficiency. The data in Table 14 indicate that the cell with the quaternary solvent electrolyte can be discharged under as high a rate as 2C with more than 96% efficiency.

Table 14

Discharge Rate Capability Test

1.4M LiPF₆/EC:DMC:EMC:DEC = 20:40:30.4:9.6

Discharge Efficiency (% of 0.2C Rate Discharge)			
0.2C	0.5C	1C	2C
100	98.6	97.7	96.4

- c) Self-Discharge/Capacity Retention Test: For cycles 10 to 12, a self-discharge/capacity retention test was carried out on the lithium ion cell. Cycle 10 (data point 84 in Fig. 8) was a normal C/5 charge and C/5 discharge cycle. In cycle 11 (data point 86 in Fig. 8), the cell was fully charged and stored on open circuit for 33 days. Then, it was discharge under a 300 mA current to 2.75V. Cycle 12 (data point 88 in Fig. 8) was performed the same as cycle 10. The self-discharge rate was calculated based on the discharge capacity ratio of cycle 11 over cycle 10. The results are listed in Table 15. The results indicate that only about 5.5% of capacity was permanently lost after 33 days of open circuit storage at room temperature under a fully charged state.

Table 15

Self-Discharge/Capacity Retention Test
1.4M LiPF₆/EC:DMC:EMC:DEC = 20:40:30.4:9.6

Self-Discharge (%)	Capacity Retention (%)
14.4	94.5

- d) Low Temperature Discharge Capability Test: For cycles 13 to 25 (curve 90 in Fig. 8), after charging, the lithium ion cell was thermally equilibrated at temperatures ranging from room temperature (RT) to -50°C for 24 hours. Then, the cell was discharged at the designated temperature under various discharge

currents until a 2.0V cut off (2.75V for RT test). The cell was further discharged to a 2.75V cut off after being warmed to room temperature for more than four hours. The discharge efficiencies under various conditions were calculated based on the ratio of discharge capacity at the assigned temperature and discharge rate over that of the total capacity of that particular cycle. The results are summarized in Table 16 and Fig. 8. The data shows that a lithium ion cell activated with the equilibrated quaternary solvent electrolyte of the present invention can be discharged at temperatures as low as -50°C under a fairly high discharge rate. High discharge efficiencies were observed.

Table 16

Low Temperature Discharge Efficiency

1.4M LiPF₆/EC:DMC:EMC:DEC = 20:40:30.4:9.6

Temperature (°C)	Discharge Rate (C)	Efficiency (% of RT)
At RT	0.2C	100.0
At -20°C	0.1C	95.2
	0.2C	95.2
	0.4C	93.9
	0.8C	92.6
	1.0C	92.0
At -30°C	0.1C	94.0
	0.2C	92.9
	0.4C	92.4
At -40°C	0.1C	91.2
	0.2C	86.0
	0.4C	83.4
At -50°C	0.1C	62.9

- e) Low Temperature Cycling Test: For cycles 26 to 65, the lithium ion cell was cycled at various temperatures. However, in this test, the cell was not only discharged at the designated temperatures, it was also charged at the same temperature. In all cycles, the cell was charged under 150 mA current (0.1C rate) to 4.1V, followed by charging the cell at 4.1V until the current dropped to 50 mA. After one hour resting on open circuit, the cell was discharged under a 300 mA current (0.2C rate) until it reached 2.0V. This occurred at the following respective temperatures: -20°C, -30°C, -37°C, or 2.75V (at RT). The beginning of the next cycle did not occur until after a one hour rest. Ten cycles were obtained respectively at -20°C, -30°C, -37°C and room temperature. The results are summarized in Fig. 8, wherein curve 92 is the results of cycling at -20°C, 94 is the results of the cycling at -30°C, curve 96 is the results of the cycling at -37°C and curve 98 is the results of the cycling at room temperature. The results indicate that a lithium ion cell activated with the quaternary solvent electrolyte of the present invention not only is capable of efficient discharged at temperatures as low as -50°C, it is also capable of being charge and discharge cycled at low temperatures (as low as -37°C tested).

From the above examples, it is clearly demonstrated that lithium ion cells activated with electrolytes comprising a quaternary mixture of EC, DMC, DEC and EMC

according to the present invention exhibit similar
cycling behavior and superior low temperature
charge/discharge capability relative to cells of a
similar electrode chemistry activated with conventional
5 solvent system electrolytes.

It is appreciated that various modifications to the
present inventive concepts described herein may be
apparent to those of ordinary skill in the art without
departing from the spirit and scope of the present
10 invention as defined by the herein appended claims.

What is claimed is:

1. An electrochemical cell, which comprises:
 - a) a negative electrode of a negative
5 electrode active material which
intercalates and deintercalates with an
alkali metal;
 - b) a positive electrode comprising an alkali
10 metal intercalated electrode active
material which intercalates and
deintercalates with the alkali metal;
 - c) an electrolyte solution activating the
negative and positive electrodes, the
15 electrolyte including an alkali metal
salt dissolved in a quaternary,
nonaqueous carbonate solvent mixture of
one cyclic carbonate and three linear
carbonates, wherein of the three linear
20 carbonates, a first linear carbonate has
the formula R^1OCOOR^1 , a second linear
carbonate has the formula R^2OCOOR^2 and a
third linear carbonate has the formula
 R^1OCOOR^2 , and wherein R^1 and R^2 are
different and are saturated or
25 unsaturated organic or inorganic groups
containing 1 to 13 carbon atoms, wherein
with the negative electrode
deintercalated with the alkali metal and
the positive electrode intercalated with
30 the alkali metal before being activated
with the electrolyte, the first, second
and third linear carbonates are in an
equilibrated ratio.

2. The electrochemical cell of claim 1 wherein the three linear carbonates are selected from the group consisting of dimethyl carbonate, diethyl carbonate, dipropyl carbonate, ethylmethyl carbonate, methylpropyl carbonate, ethylpropyl carbonate, and mixtures thereof.

3. The electrochemical cell of claim 1 wherein the one cyclic carbonate is selected from the group consisting of ethylene carbonate, propylene carbonate, butylene carbonate, vinylene carbonate, and mixtures thereof.

4. The electrochemical cell of claim 1 wherein the electrolyte comprises ethylene carbonate, dimethyl carbonate, ethylmethyl carbonate and diethyl carbonate.

5. The electrochemical cell of claim 4 wherein the ethylene carbonate is in the range of about 20% to about 50%, the dimethyl carbonate is in the range of about 12% to about 75%, the ethylmethyl carbonate is in the range of about 5% to about 45%, and the diethyl carbonate is in the range of about 3% to about 45%, by volume.

6. The electrochemical cell of claim 1 wherein the negative electrode active material is selected from the group consisting of coke, carbon black, graphite, acetylene black, carbon fibers, glassy carbon, and mixtures thereof.

7. The electrochemical cell of claim 1 wherein the alkali metal intercalated electrode active material is selected from the group consisting of lithiated oxides, lithiated sulfides, lithiated selenides and lithiated tellurides of the group selected from vanadium,

titanium, chromium, copper, molybdenum, niobium, iron, nickel, cobalt, manganese, and mixtures thereof.

8. An electrochemical cell, which comprises:

- 5 a) a negative electrode of a negative electrode active material which intercalates and deintercalates with lithium;
- 10 b) a positive electrode comprising a lithiated electrode active material which intercalates and deintercalates with lithium; and
- 15 c) an electrolyte solution activating the negative and positive electrodes, the electrolyte including an alkali metal salt dissolved in a quaternary, nonaqueous carbonate solvent mixture of ethylene carbonate, dimethyl carbonate, ethylmethyl carbonate and diethyl
- 20 carbonate, wherein with the negative electrode deintercalated with lithium and the positive electrode intercalated with lithium before being activated with the electrolyte, the dimethyl carbonate, the
- 25 ethylmethyl carbonate and the diethyl carbonate are in an equilibrated ratio.

9. The electrochemical cell of claim 8 wherein the ethylene carbonate is in the range of about 20% to about

30 50%, the dimethyl carbonate is in the range of about 12% to about 75%, the ethylmethyl carbonate is in the range of about 5% to about 45%, and the diethyl carbonate is in the range of about 3% to about 45%, by volume.

10. The electrochemical cell of claim 8 wherein the electrolyte includes an alkali metal salt selected from the group consisting of LiPF_6 , LiBF_4 , LiAsF_6 , LiSbF_6 , LiClO_4 , LiAlCl_4 , LiGaCl_4 , LiNO_3 , $\text{LiC}(\text{SO}_2\text{CF}_3)_3$, $\text{LiN}(\text{SO}_2\text{CF}_3)_2$,
5 LiSCN , $\text{LiO}_3\text{SCF}_2\text{CF}_3$, $\text{LiC}_6\text{F}_5\text{SO}_3$, LiO_2CCF_3 , LiSO_3F , $\text{LiB}(\text{C}_6\text{H}_5)_4$, LiCF_3SO_3 , and mixtures thereof.

11. The electrochemical cell of claim 8 wherein the negative electrode active material is selected from the
10 group consisting of coke, carbon black, graphite, acetylene black, carbon fibers, a glassy carbon, and mixtures thereof.

12. The electrochemical cell of claim 8 wherein the
15 negative electrode active material is mixed with a fluoro-resin binder.

13. The electrochemical cell of claim 8 wherein the lithiated electrode active material is selected from the
20 group consisting of lithiated oxides, lithiated sulfides, lithiated selenides and lithiated tellurides of the group selected from vanadium, titanium, chromium, copper, molybdenum, niobium, iron, nickel, cobalt, manganese, and mixtures thereof.

25

14. The electrochemical cell of claim 13 wherein the lithiated electrode active material is mixed with a fluoro-resin binder.

30 15. The electrochemical cell of claim 13 wherein the lithiated electrode active material is mixed with a conductive addition selected from the group consisting of acetylene black, carbon black, graphite, nickel

powder, aluminum powder, titanium powder, stainless steel powder, and mixtures thereof.

16. An electrochemical cell, which comprises:

- 5 a) a negative electrode of a carbonaceous material which intercalates and deintercalates with lithium;
- b) a positive electrode comprising lithium cobalt oxide which intercalates and
10 deintercalates with lithium; and
- c) an electrolyte solution activating the negative electrode and the positive
 electrode, the electrolyte including a lithium salt dissolved in a quaternary,
15 nonaqueous carbonate solvent mixture of ethylene carbonate, dimethyl carbonate,
 ethylmethyl carbonate and diethyl carbonate, wherein with the negative
 electrode deintercalated with lithium and
20 the positive electrode intercalated with lithium before being activated with the
 electrolyte, the dimethyl carbonate, the ethylmethyl carbonate and the diethyl
 carbonate are in an equilibrated ratio.

25

17. A method for providing an electrochemical cell, comprising the steps of:

- a) providing a negative electrode comprising
 a negative electrode active material
30 which intercalates and deintercalates with an alkali metal;
- b) providing a positive electrode comprising an alkali metal intercalated electrode

- active material which intercalates and deintercalates with the alkali metal;
- c) providing an electrolyte including an alkali metal salt dissolved in a quaternary, nonaqueous carbonate solvent mixture of one cyclic carbonate and three linear carbonates, wherein of the three linear carbonates, a first linear carbonate has the formula R^1OCOOR^1 , a second linear carbonate has the formula R^2OCOOR^2 and a third linear carbonate has the formula R^1OCOOR^2 , and wherein R^1 and R^2 are different and are saturated or unsaturated organic or inorganic groups containing 1 to 13 carbon atoms; and
- d) assembling the negative electrode deintercalated with the alkali metal and the positive electrode intercalated with the alkali metal before activating the negative electrode and the positive electrode with the electrolyte having the three linear carbonates in an equilibrated ratio.

18. The method of claim 17 including selecting the three linear carbonates from the group consisting of dimethyl carbonate, diethyl carbonate, dipropyl carbonate, ethylmethyl carbonate, methylpropyl carbonate, ethylpropyl carbonate, and mixtures thereof.

19. The method of claim 17 including selecting the one cyclic carbonate from the group consisting of ethylene carbonate, propylene carbonate, butylene carbonate, vinylene carbonate, and mixtures thereof.

20. The method of claim 17 including providing the nonaqueous carbonate solvent mixture comprising ethylene carbonate, dimethyl carbonate, ethylmethyl carbonate and diethyl carbonate.

5

21. The method of claim 20 wherein the ethylene carbonate is in the range of about 20% to about 50%, the dimethyl carbonate is in the range of about 12% to about 75%, the ethylmethyl carbonate is in the range of about 5% to about 45%, and the diethyl carbonate is in the range of about 3% to about 45%, by volume.

10

22. The method of claim 17 including selecting the negative electrode active material from the group consisting of coke, carbon black, graphite, acetylene black, carbon fibers, glassy carbon, and mixtures thereof.

15

23. The method of claim 17 including selecting the lithiated electrode active material from the group consisting of lithiated oxides, lithiated sulfides, lithiated selenides and lithiated tellurides of the group selected from vanadium, titanium, chromium, copper, molybdenum, niobium, iron, nickel, cobalt, manganese, and mixtures thereof.

20

25

24. A method for providing an electrochemical cell, comprising the steps of:

30

- a) providing a negative electrode comprising a negative electrode active material which intercalates and deintercalates with lithium;
- b) providing a positive electrode comprising a lithiated electrode active material

which intercalates and deintercalates with lithium; and

5 c) providing an electrolyte including an alkali metal salt dissolved in a quaternary, nonaqueous carbonate solvent mixture of ethylene carbonate, dimethyl carbonate, ethylmethyl carbonate and diethyl carbonate; and

10 d) assembling the cell having the negative electrode deintercalated with the lithium and the positive electrode intercalated with lithium before activating the negative electrode and the positive electrode with the electrolyte having the
15 dimethyl carbonate, the ethylmethyl carbonate and the diethyl carbonate in an equilibrated ratio.

25 25. The method of claim 24 wherein the ethylene carbonate is in the range of about 20% to about 50%, the dimethyl carbonate is in the range of about 12% to about 75%, the ethylmethyl carbonate is in the range of about 5% to about 45%, and the diethyl carbonate is in the range of about 3% to about 45%, by volume.

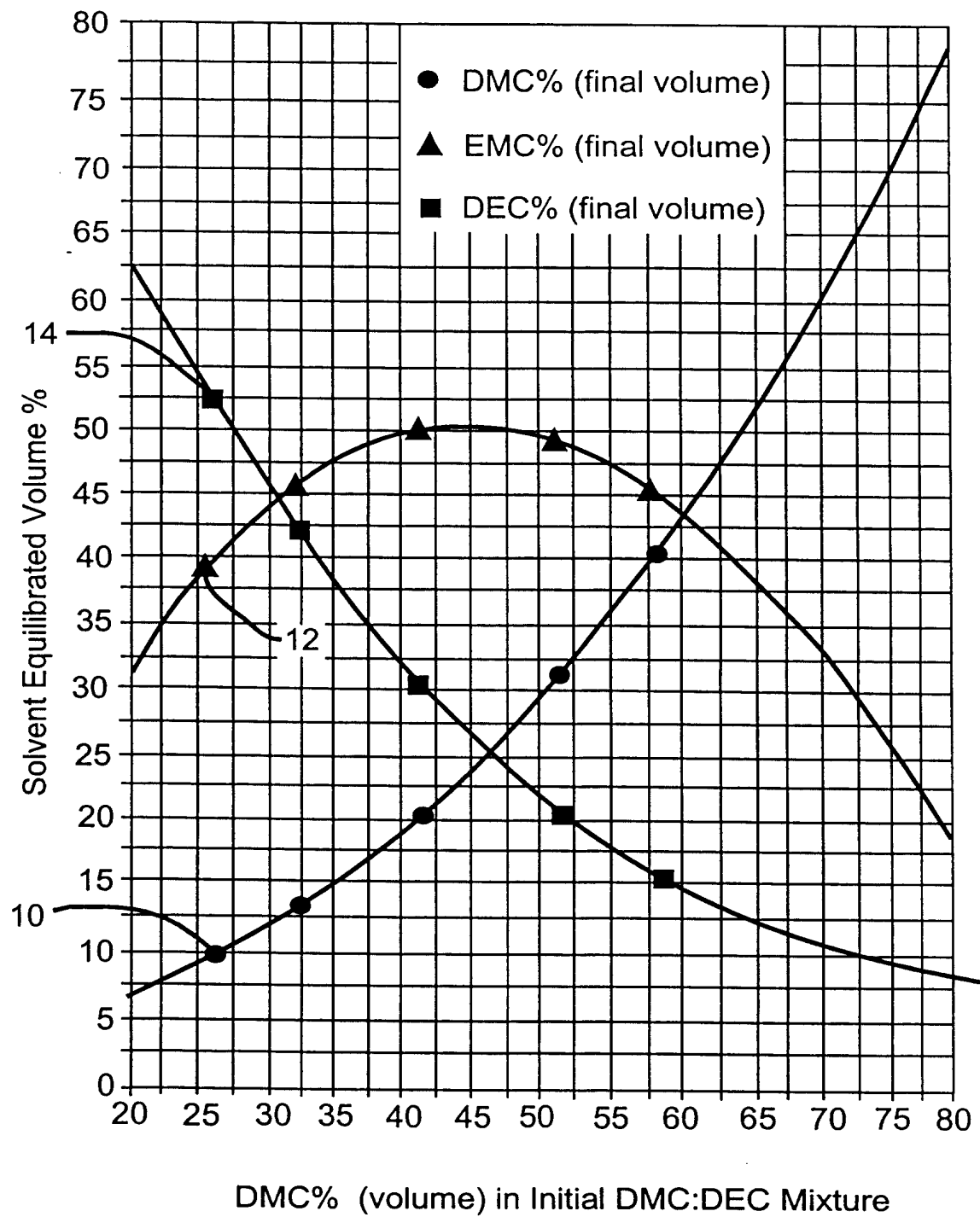
26. The method of claim 24 wherein the alkali metal salt is selected from the group consisting of LiPF_6 , LiBF_4 , LiAsF_6 , LiSbF_6 , LiClO_4 , LiAlCl_4 , LiGaCl_4 , LiNO_2 , $\text{LiC}(\text{SO}_2\text{CF}_3)_3$, $\text{LiN}(\text{SO}_2\text{CF}_3)_2$, LiSCN , $\text{LiO}_3\text{SCF}_2\text{CF}_3$, $\text{LiC}_6\text{F}_5\text{SO}_3$,
30 LiO_2CCF_3 , LiSO_3F , $\text{LiB}(\text{C}_6\text{H}_5)_4$, LiCF_3SO_3 , and mixtures thereof.

27. The method of claim 24 including selecting the negative electrode active material from the group

- 45 -

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consisting of coke, carbon black, graphite, acetylene black, carbon fibers, glassy carbon, and mixtures thereof.



—FIG.1

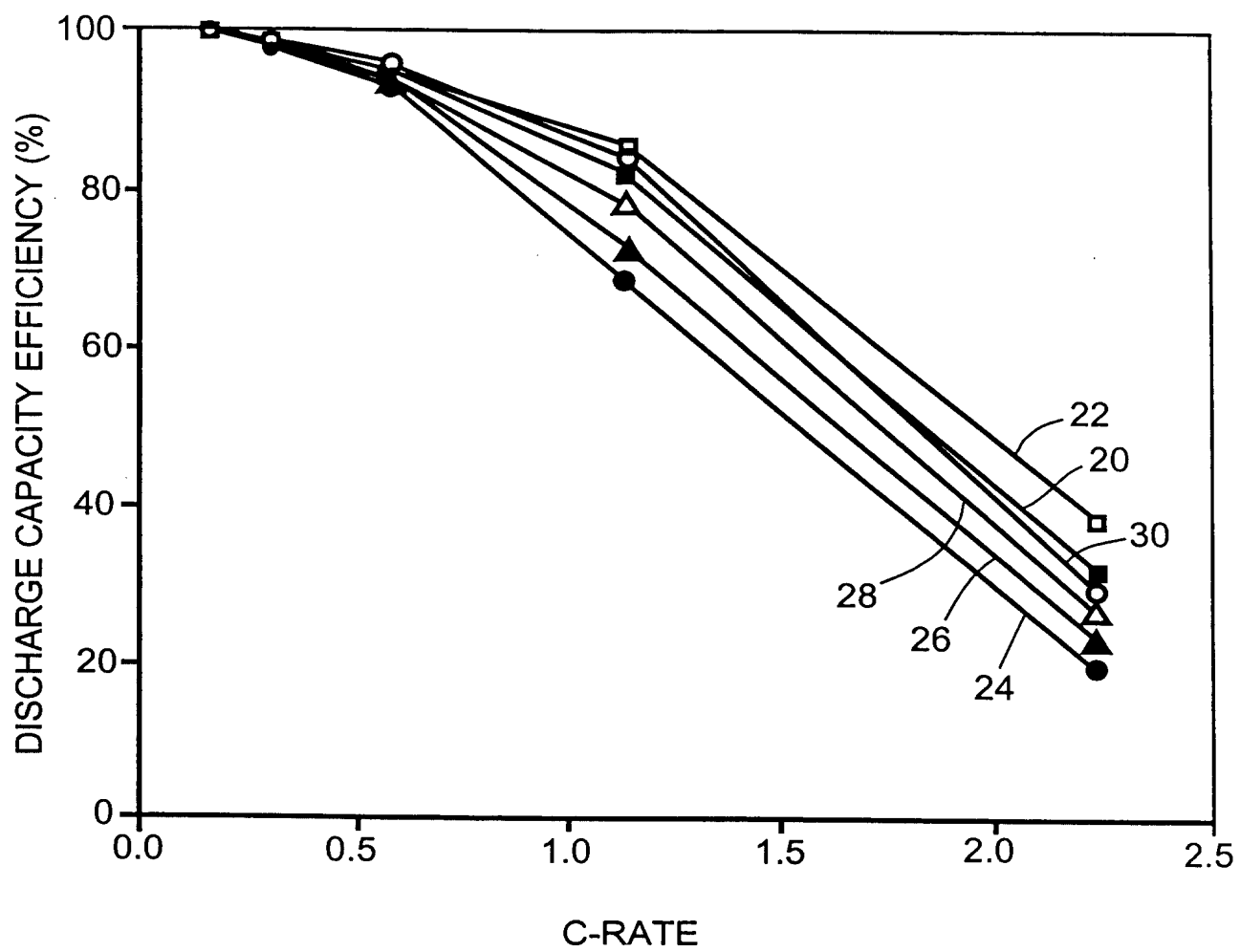
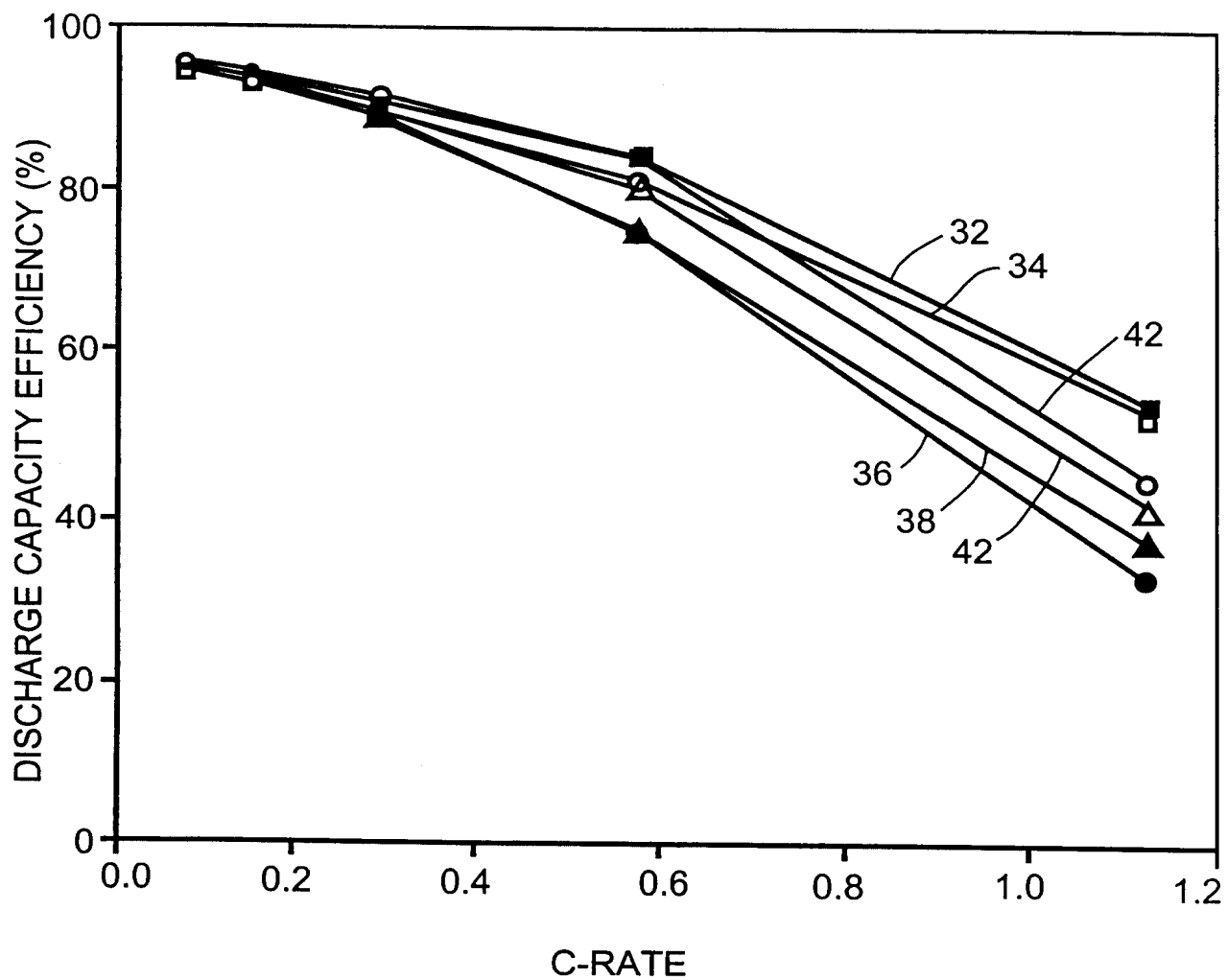
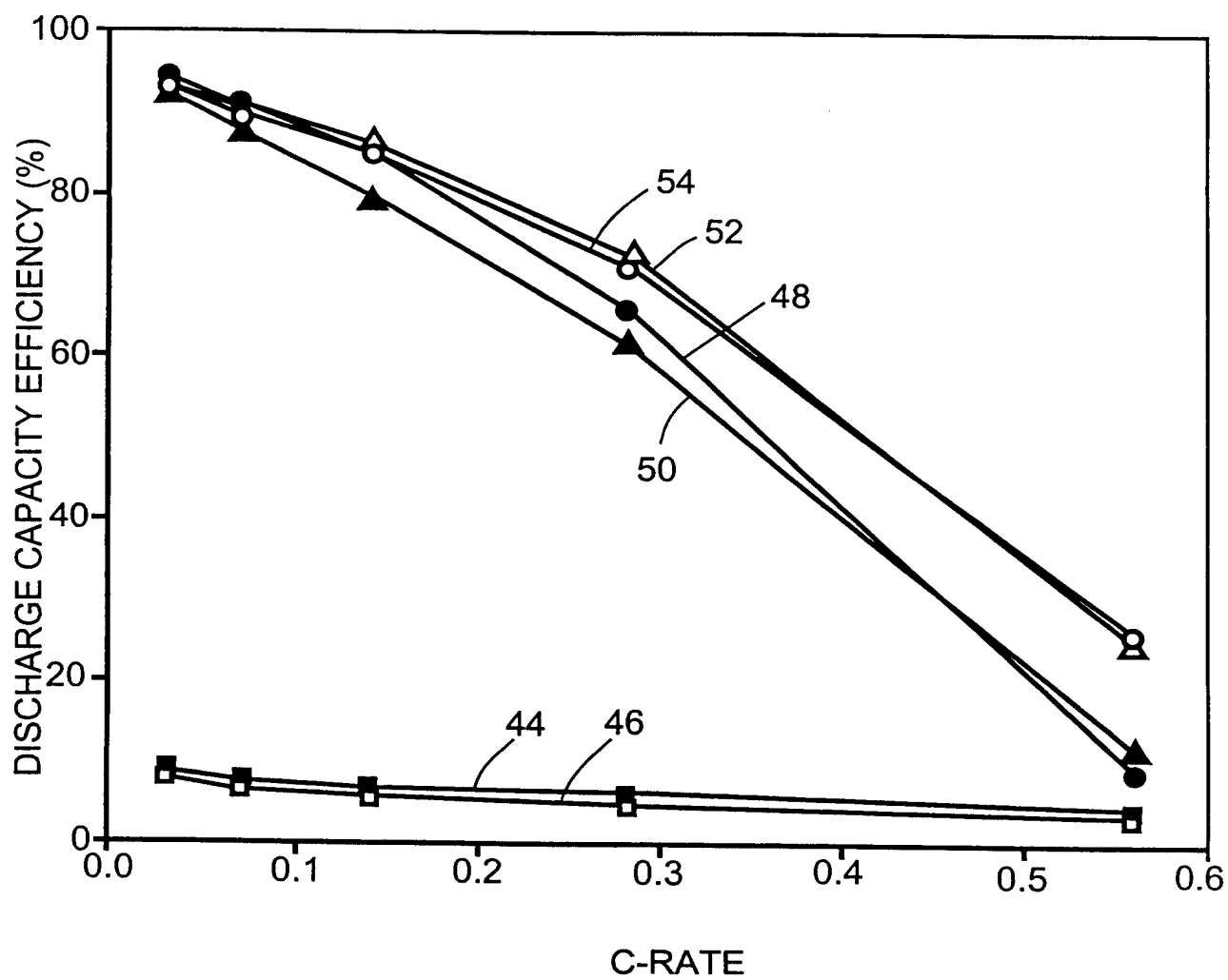


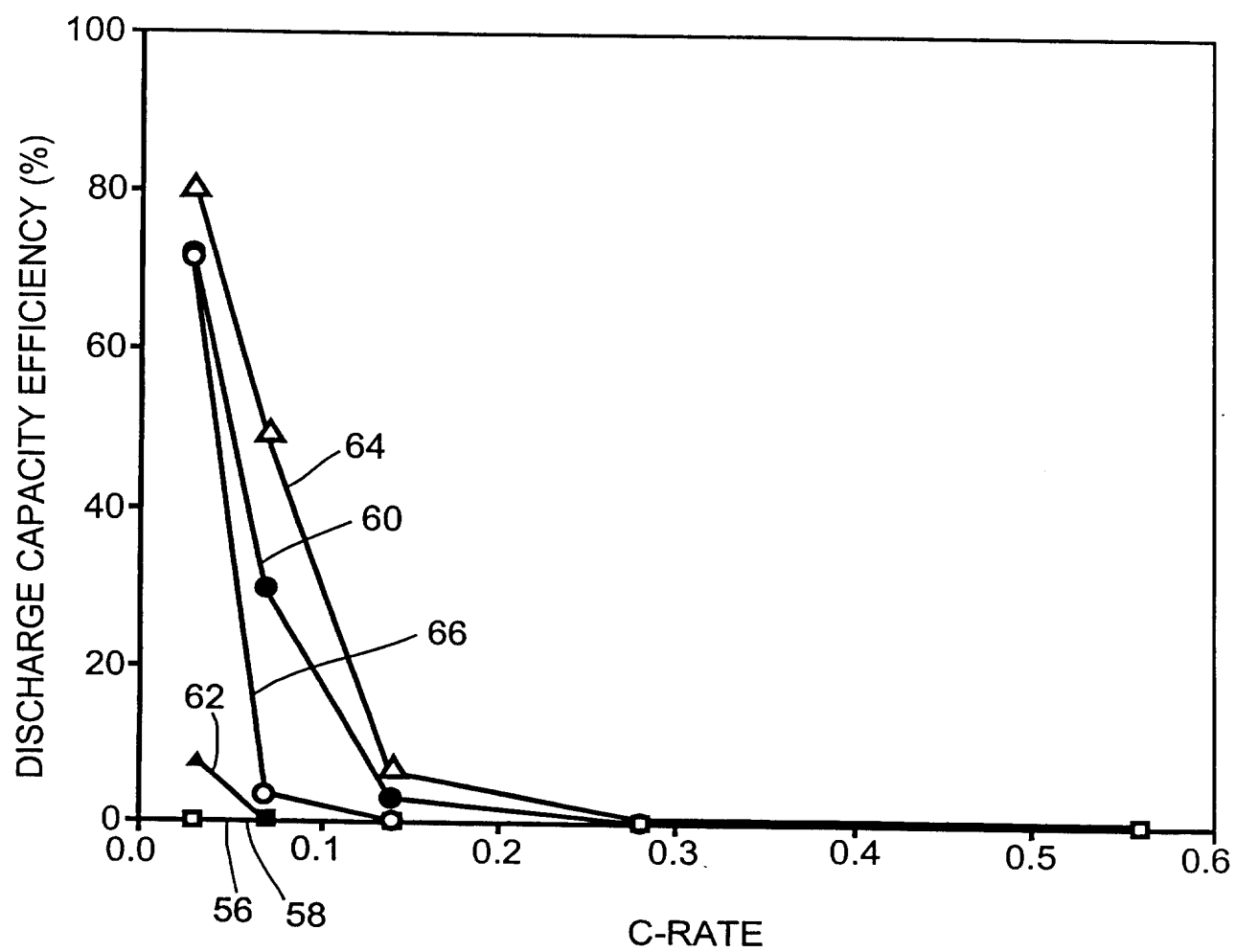
FIG. 2



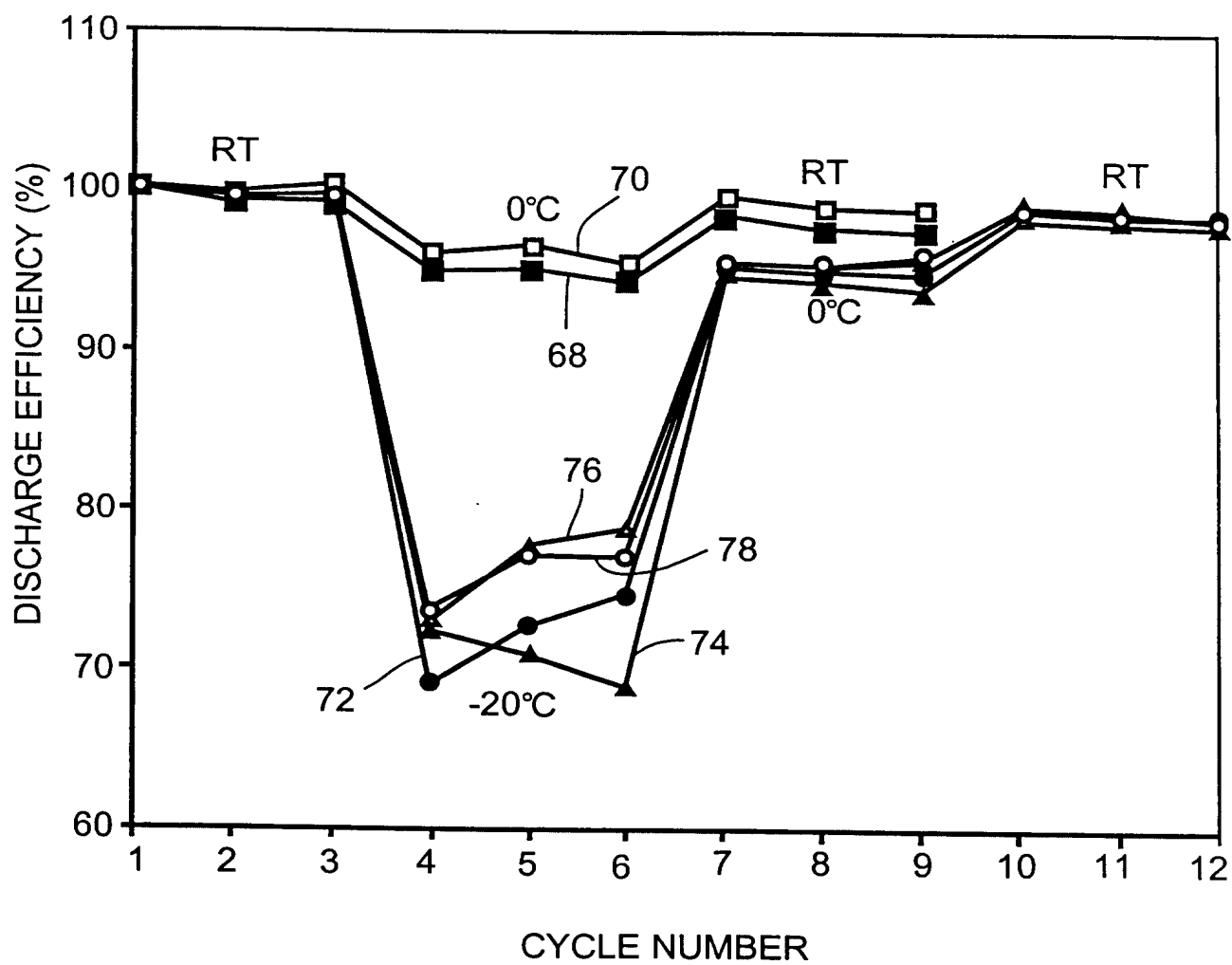
—FIG. 3



—FIG. 4



—FIG.5



—FIG.6

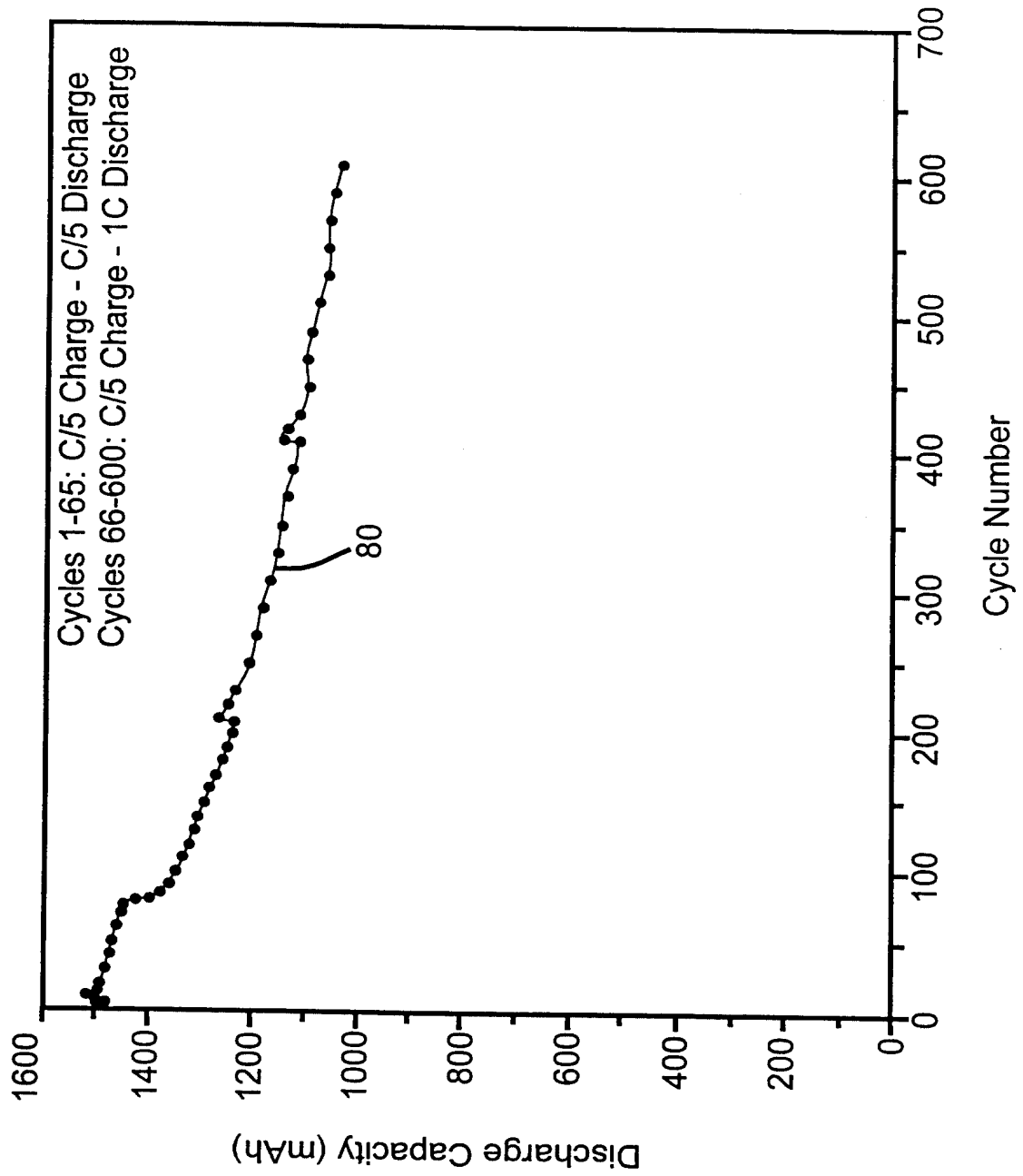


FIG. 7

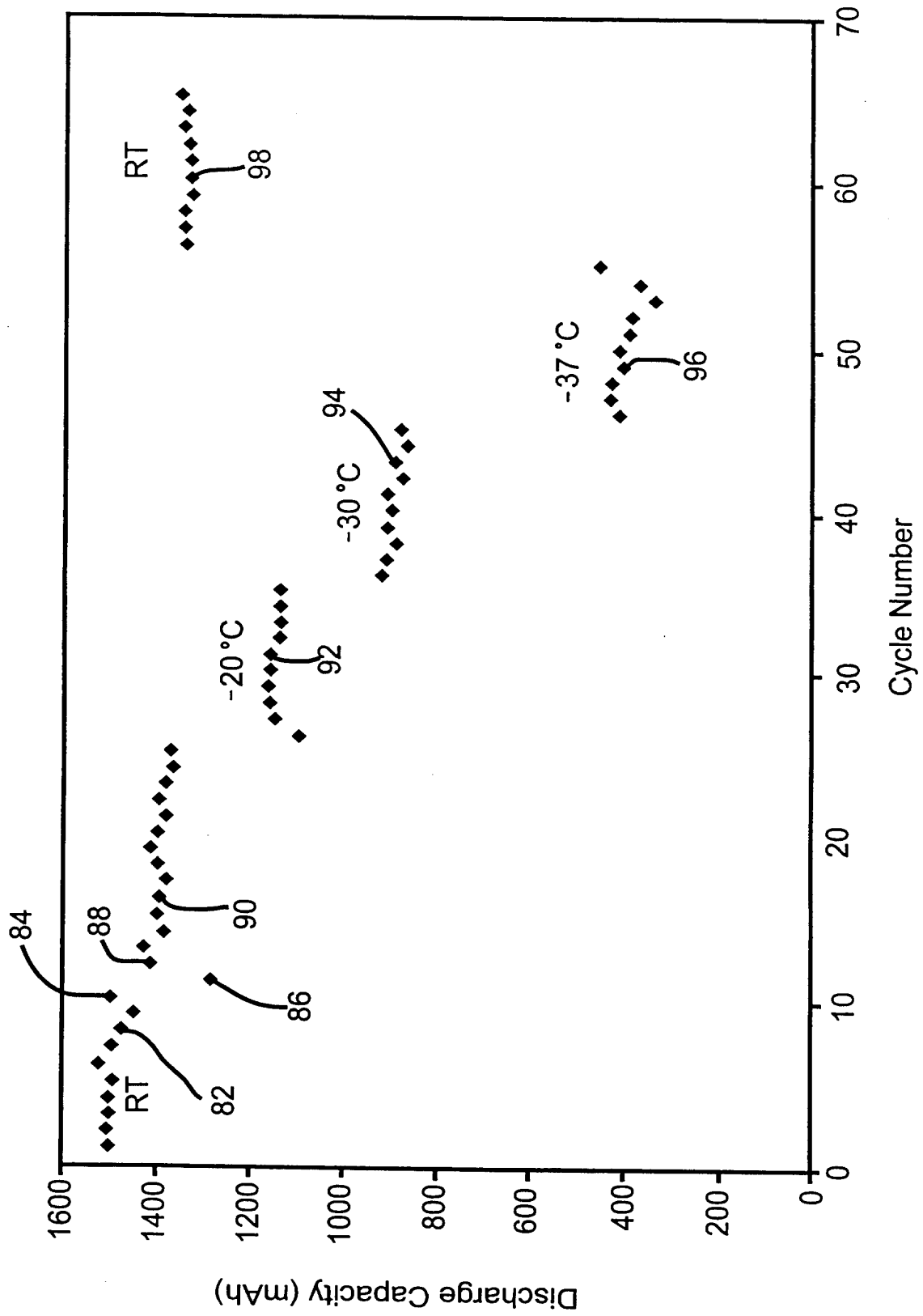
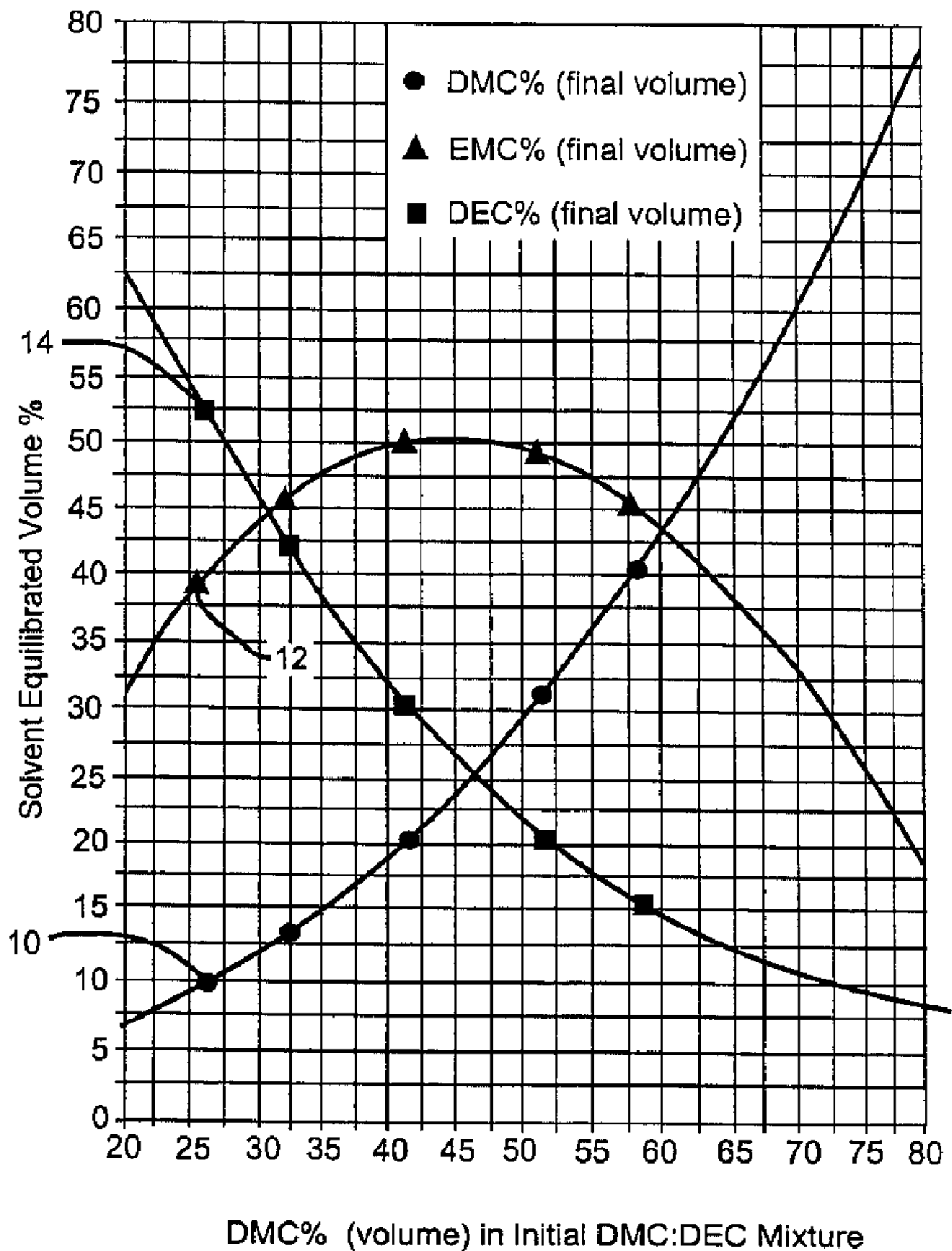


FIG. 8



DERWENT-ACC-NO: 2002-491014**DERWENT-WEEK: 200373*****COPYRIGHT 2009 DERWENT INFORMATION LTD***

TITLE: Electrochemical cell e.g. lithium ion cell has cathode, alkali metal intercalated anode electroactive materials and electrolyte comprising alkali metal salt dissolved in quaternary non-aqueous carbonate solvent mixture

INVENTOR: GAN H; TAKEUCHI E S**PATENT-ASSIGNEE: GREATBATCH LTD WILSON[GREW]****PRIORITY-DATA: 2000US-669936 (September 26, 2000)****PATENT-FAMILY:**

PUB-NO	PUB-DATE	LANGUAGE
CA 2334054 A1	March 26, 2002	EN
JP 2002117898 A	April 19, 2002	JA
KR 2002024770 A	April 1, 2002	KO
TW 529198 A	April 21, 2003	ZH

APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
CA 2334054A1	N/A	2001CA-2334054	February 2, 2001
TW 529198A	N/A	2001TW-101789	January 30, 2001
KR2002024770A	N/A	2001KR-033449	June 14, 2001
JP2002117898A	N/A	2001JP-237703	August 6, 2001

INT-CL-CURRENT:

TYPE	IPC DATE
CIPP	H01M10/40 20060101
CIPS	H01M10/26 20060101
CIPS	H01M4/02 20060101
CIPS	H01M4/58 20060101
CIPS	H01M4/60 20060101
CIPS	H01M4/62 20060101

RELATED-ACC-NO: 2000-162967 2001-060083 2003-670780

ABSTRACTED-PUB-NO: CA 2334054 A1

BASIC-ABSTRACT:

NOVELTY - An electrochemical cell has cathode and alkali metal intercalated anode electroactive materials which intercalates and deintercalates with an alkali metal. The electrolyte solution activates the electrodes and includes an alkali metal salt dissolved in a quaternary, non-aqueous carbonate solvent mixture of one cyclic carbonate and three linear carbonates.

DESCRIPTION - An electrochemical cell comprises anode, cathode and electrolyte solution. The cathode comprises negative electroactive material which intercalates and deintercalates with an alkali metal. The anode comprises an alkali metal intercalated electroactive material which intercalates and deintercalates with an alkali metal. The electrolyte solution activates the electrodes and includes an alkali metal salt dissolved in a quaternary, non-aqueous carbonate solvent mixture of one cyclic carbonate and three linear carbonates. The first linear carbonate is R1OCOOR1, the second linear carbonate is R2OCOOR2 and the third linear carbonate is R1OCOOR2.

R1 and R2 = 1-13C (in)organic optionally saturated groups.

The linear carbonates are in an equilibrated ratio when the cathode is deintercalated with alkali metal and anode is intercalated with alkali metal before being activated. An

INDEPENDENT CLAIM is included for a method for providing an electrochemical cell by assembling the cathode, deintercalated with alkali metal and anode, intercalated with alkali metal prior to activating the electrodes with the electrolyte having the linear carbonates in an equilibrated ratio.

USE - As electrochemical cells such as lithium ion cell.

ADVANTAGE - The lithium ion cells activated with the electrolyte have good room temperature cyclic characteristics and excellent low temperature discharge behavior. Graphite has relatively high lithium retention capacity. Fibers of carbonaceous material have excellent mechanical properties which permit them to be fabricated into rigid electrodes capable of withstanding degradation during repeated charging discharging cyclic. The organic carbonates exhibit high oxidative stability towards cathode material and good kinetic stability towards anode material.

DESCRIPTION OF DRAWING(S) - The figure shows the graph of equilibrated mixtures of DMC:EMC:DEC based on a starting mixture of DMC:DEC.

EQUIVALENT-ABSTRACTS:

INORGANIC CHEMISTRY

Preferred Composition: The cathode comprises carbonaceous material and the cathode active material intercalates and deintercalates with lithium. The anode comprises lithiated electroactive material, preferably lithium cobalt oxide which intercalates and deintercalates with lithium.

Preferred Component: The non-aqueous carbonate solvent mixture of the electrolyte comprises ethylene carbonate (in volume%) (20-50), dimethyl carbonate (12-75), ethylmethyl carbonate (5-45), and diethyl carbonate (3-45).

Preferred Material: The cathode active material is coke, carbon black, graphite, acetylene black, carbon fibers and glassy carbon and is mixed with fluororesin binder. The alkali metal intercalated electroactive material is lithiated oxides, lithiated sulfides, lithiated selenides and lithiated tellurides selected from

vanadium, titanium, chromium, copper, molybdenum, niobium, iron, nickel, cobalt, and manganese and is mixed with fluoro-resin binder and conductive additive such as acetylene black, carbon black, graphite, nickel powder, aluminum powder and stainless steel powder.

SPECIFIC MATERIALS

The alkali metal salt in the electrolyte is LiPF_6 , LiBF_4 , LiAsF_6 , LiSbF_6 , LiClO_4 , LiAlCl_4 , LiGaCl_4 , LiNO_3 , $\text{Li}(\text{SO}_2\text{CF}_3)_3$, $\text{LiN}(\text{SO}_2\text{CF}_3)_2$, LiSCN , $\text{LiO}_3\text{SCF}_2\text{CF}_3$, $\text{LiC}_6\text{F}_5\text{SO}_3$, LiO_2CCF_3 , LiSO_3F , $\text{LiB}(\text{C}_6\text{H}_5)_4$ and LiCF_3SO_3 .

SPECIFIC COMPOUNDS

The three linear carbonates are dimethyl carbonate, diethyl carbonate, dipropyl carbonate, ethylmethyl carbonate, methylpropyl carbonate, and ethylpropyl carbonate. The cyclic carbonate is ethylene carbonate, propylene carbonate, butylene carbonate and vinylene carbonate.

An electrolyte containing ethylene carbonate (EC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC) in a solvent ratio of 20:32:36:12 and 1M of LiAsF_6 was prepared. Conductivity of the electrolyte (in ms) was recorded from -20 - 50 degreesC with YSI model 32 conductivity meter and was respectively 3.04, 4.22, 5.59, 6.95, 8.59, 10.01, 11.80 and 13.35. The conductivity results indicated that at low temperatures, electrolyte conductivity was inversely proportional to the EC percentage. Smaller the linear carbonate molecular size, the lower the solvent viscosity and the higher the electrolyte conductivity. The electrolyte had a freezing point of -55 degreesC is less than -50 degreesC. A cathode was prepared by casting a LiCoO_2 cathode mixture on an aluminum foil. The cathode mix contained 91% LiCoO_2 , 6% graphite additive and 3% polyvinylidene fluoride (PVDF) binder. The anode was prepared similarly by casting an anode mixture containing 91.7% graphite and 8.3% PVDF binder on a copper foil. An electrode assembly was obtained by placing one layer of polyethylene separator between the electrodes. The assembly was spirally wound into a jellyroll configuration and housed inside an AA sized cylindrical stainless steel casing. The fabricated cells were charge/discharge cycled between 4.1v and 2.75V under a 0.14C

discharge rate (1C rate = 520 mA) at room temperature. The cells were charged under 0.14C rate to 4.1V and then held at that voltage until the current dropped to 10% of the original current. The cell had discharge capacities (in mAh) of respectively 520, 492, and 553 during the 1st, 10th and 50th cycle. The capacity retention (in%) at 50th cycle Vs cycle 1 was 87.1 and Vs cycle 10 was 92.1.

CHOSEN-DRAWING: Dwg.1/8

**TITLE-TERMS: ELECTROCHEMICAL CELL LITHIUM ION
CATHODE ALKALI METAL INTERCALATED
ANODE MATERIAL ELECTROLYTIC
COMPRISE SALT DISSOLVE QUATERNARY
NON AQUEOUS CARBONATE SOLVENT
MIXTURE**

DERWENT-CLASS: E19 L03 X16

**CPI-CODES: E05-A; E05-C02; E07-A04; E10-A11B2; E31-C;
E31-F05; E31-K07; E31-L; E31-M; E31-Q02;
E33-G; E34-C03; E35-F; L03-E01B5B;**

EPI-CODES: X16-B01F1; X16-E08A; X16-J07;

**CHEMICAL-CODES: Chemical Indexing M3 *01* Fragmentation
Code K0 L4 L472 M210 M211 M272 M282
M320 M416 M620 M782 Q454 R023 Specific
Compounds R07250 Registry Numbers 815**

**Chemical Indexing M3 *02* Fragmentation
Code K0 L4 L472 M210 M212 M272 M282
M320 M416 M620 M782 Q454 R023 Specific
Compounds R21644 Registry Numbers 530**

**Chemical Indexing M3 *03* Fragmentation
Code K0 L4 L472 M210 M213 M231 M272
M282 M320 M416 M620 M782 Q454 R023
Specific Compounds RA00AY Registry
Numbers 200563**

**Chemical Indexing M3 *04* Fragmentation
Code K0 L4 L472 M210 M211 M212 M272
M282 M320 M416 M620 M782 Q454 R023
Specific Compounds RA00AM Registry**

Numbers 193936

**Chemical Indexing M3 *05* Fragmentation
Code K0 L4 L472 M210 M211 M213 M231
M272 M282 M320 M416 M620 M782 Q454
R023 Specific Compounds RA00AW Registry
Numbers 200561**

**Chemical Indexing M3 *06* Fragmentation
Code K0 L4 L472 M210 M212 M213 M231
M272 M282 M320 M416 M620 M782 Q454
R023 Specific Compounds RA00AX Registry
Numbers 200562**

**Chemical Indexing M3 *07* Fragmentation
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M413 M510 M521 M530 M540 M782 Q454
R023 Specific Compounds R00645 Registry
Numbers 826**

**Chemical Indexing M3 *08* Fragmentation
Code F012 F014 F140 J5 J521 L9 L922 M210
M211 M240 M281 M320 M413 M510 M521
M530 M540 M782 Q454 R023 Specific
Compounds R00844 Registry Numbers 1956**

**Chemical Indexing M3 *09* Fragmentation
Code F012 F014 F015 F140 J5 J521 L9 L922
M210 M211 M240 M282 M320 M413 M510
M521 M530 M540 M782 Q454 R023 Specific
Compounds R10130 Registry Numbers
131171**

**Chemical Indexing M3 *10* Fragmentation
Code F012 F014 F140 J5 J521 L9 L922 M210
M212 M240 M281 M320 M413 M510 M521
M530 M540 M782 Q454 R023 Specific
Compounds RA1925 Registry Numbers
259868**

**Chemical Indexing M3 *11* Fragmentation
Code F012 F140 J5 J521 L9 L922 M280 M320
M413 M510 M521 M530 M540 M782 Q454**

**R023 Specific Compounds RA09RP Registry
Numbers 22497**

**Chemical Indexing M3 *12* Fragmentation
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M210 M211 M212 M213 M214 M215 M216
M220 M221 M222 M223 M224 M225 M226
M231 M232 M233 M272 M282 M320 M416
M620 M782 Q454 R023 Markush Compounds
006647401**

**Chemical Indexing M3 *13* Fragmentation
Code F012 F014 F015 F017 F019 F140 J5
J521 L9 L922 M210 M211 M212 M213 M214
M215 M216 M220 M221 M222 M223 M224
M225 M226 M231 M232 M233 M240 M280
M281 M282 M283 M320 M413 M510 M521
M530 M540 M782 Q454 R023 Markush
Compounds 006647402**

**Chemical Indexing M3 *14* Fragmentation
Code A103 A940 B115 B720 B752 B819 B831
C009 C100 C803 C804 C805 C806 C807 M411
M782 Q454 R023 Specific Compounds
R10929 Registry Numbers 131494**

**Chemical Indexing M3 *15* Fragmentation
Code A103 A940 B105 B720 B752 B809 B831
C009 C100 C803 C804 C805 C806 C807 H607
M411 M782 Q454 R023 Specific Compounds
R07048 RA03PB Registry Numbers 1025**

**Chemical Indexing M3 *16* Fragmentation
Code A103 A351 A940 A980 C009 C100 C730
C801 C803 C804 C805 C806 C807 M411 M782
Q454 R023 Specific Compounds R19040
Registry Numbers 134243**

**Chemical Indexing M3 *17* Fragmentation
Code A103 A940 C017 C108 C300 C730 C801
C803 C804 C805 C807 M411 M782 Q454 R023
Specific Compounds R01826 Registry
Numbers 166**

Chemical Indexing M3 *18* Fragmentation
Code A103 A313 A940 A980 C017 C100 C730
C801 C803 C805 C806 C807 M411 M782 Q454
R023 Specific Compounds R08552 Registry
Numbers 131499

Chemical Indexing M3 *19* Fragmentation
Code A103 A331 A940 C009 C100 C730 C801
C803 C804 C805 C806 C807 M411 M782 Q454
R023 Specific Compounds RA7E7L Registry
Numbers 557158

Chemical Indexing M3 *20* Fragmentation
Code A103 A940 C108 C307 C510 C730 C801
C802 C803 C804 C807 M411 M782 Q454 R023
Specific Compounds R01821 Registry
Numbers 2963

Chemical Indexing M3 *21* Fragmentation
Code A103 A940 C106 C107 C116 C520 C730
C801 C802 C803 C806 M411 M782 Q454 R023
Specific Compounds R16740 Registry
Numbers 133545

Chemical Indexing M3 *22* Fragmentation
Code A103 A970 B505 B720 B744 B770 B809
B831 C710 G018 G019 G100 H6 H601 H607
H609 H643 M1 M121 M129 M144 M280 M320
M411 M510 M520 M533 M540 M782 Q454
R023 Specific Compounds RA0LXJ Registry
Numbers 229307

Chemical Indexing M3 *23* Fragmentation
Code A103 A960 C710 H6 H607 H685 K0 K4
K431 K432 M280 M311 M321 M344 M362
M391 M411 M510 M520 M530 M540 M620
M630 M782 Q454 R023 Specific Compounds
R07047 RA00NL Registry Numbers 2989

Chemical Indexing M3 *24* Fragmentation
Code A103 A960 C710 H6 H607 H685 J0 J011
J1 J171 M280 M311 M321 M344 M349 M362

**M391 M411 M510 M520 M530 M540 M620
M630 M782 Q454 R023 Specific Compounds
R22121 Registry Numbers 2276**

**Chemical Indexing M3 *25* Fragmentation
Code A103 A960 C316 C710 H6 H685 H689
K0 K4 K442 K499 L6 L620 M280 M311 M323
M343 M344 M362 M383 M391 M393 M411
M510 M520 M530 M540 M620 M630 M782
Q454 R023 Specific Compounds RA2UWV
Registry Numbers 338496**

**Chemical Indexing M3 *26* Fragmentation
Code A103 A960 C316 C710 H6 H607 H685
H689 K0 K3 K352 K399 M280 M311 M322
M344 M362 M392 M411 M510 M520 M530
M540 M620 M630 M782 Q454 R023 Specific
Compounds RA0AWK Registry Numbers
12158**

**Chemical Indexing M3 *27* Fragmentation
Code A103 A960 C710 H6 H601 H607 H608
H684 H685 K0 K4 K431 K432 M280 M312
M321 M332 M344 M362 M391 M411 M510
M520 M530 M540 M620 M630 M782 Q454
R023 Specific Compounds RA0DGZ Registry
Numbers 218227**

**Chemical Indexing M3 *28* Fragmentation
Code A103 A960 C710 G018 G100 H6 H601
H607 H609 H643 K0 K4 K431 K432 M280
M320 M411 M510 M520 M531 M540 M630
M782 Q454 R023 Specific Compounds
RA1DAA Registry Numbers 265409**

**Chemical Indexing M3 *29* Fragmentation
Code A103 A940 C009 C100 C101 C108 C316
C730 C801 C803 C804 C805 M411 M782 Q454
R023 Specific Compounds RA1DAD Registry
Numbers 265412**

**UNLINKED-DERWENT-REGISTRY-
NUMBERS:**

**; 0645U ; 0844U ; 1821U ;
1826U**

SECONDARY-ACC-NO:

CPI Secondary Accession Numbers: 2002-139464

Non-CPI Secondary Accession Numbers: 2002-388145